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PROCEEDINGS

OF THE

ROYAL SOCIETY OF LONDON

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND PHYSICAL CHARACTER.

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MINUTES OF MEETINGS.—SESSION 1906–7.

November 1, 1906.

Sir W. D. NIVEN, Vice-President, in the Chair.

Professor Archibald B. Macallum was admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Right Hon. Richard Burdon Haldane and the Right Hon. Viscount Iveagh were balloted for and elected Fellows of the Society.

The following Papers, received during the Recess, and published or in course of publication, in accordance with the Standing Orders of Council, were read in title:—

"*Glossina palpalis* in its Relation to *Trypanosoma gambiense* and other Trypanosomes (Preliminary Report)." By E. A. MINCHIN, M.A., Lieutenant A. C. H. GRAY, R.A.M.C., and the late Lieutenant F. M. G. TULLOCH, R.A.M.C. (Sleeping Sickness Commission).

"A Method for determining Velocities of Saponification." By Professor JAMES WALKER, F.R.S.

The following Papers were read:—

I. "On Intravascular Coagulation in Albinoes and Pigmented Animals, and on the Behaviour of the Nucleo-proteids of Testes in Solution in the Production of Intravascular Coagulation." By G. P. MUDGE. Communicated by Dr. A. D. WALLER, F.R.S.

II. "Nitrification of Sewage." By Dr. G. REID. Communicated by Professor F. GOTCH, F.R.S.

III. "A General Consideration of the Subaerial and Fresh-water Algal Flora of Ceylon." By Dr. F. E. FRITSCH. Communicated by Professor F. W. OLIVER, F.R.S.

IV. "The Anæsthetic and Lethal Quantity of Chloroform in the Blood of Animals." By Dr. G. A. BUCKMASTER and J. A. GARDNER. Communicated by Dr. A. D. WALLER, F.R.S.

November 8, 1906.

Lord RAYLEIGH, O.M., D.C.L., President, in the Chair

The Right Hon. Richard Burdon Haldane and the Right Hon. Viscount Iveagh were admitted into the Society.

His Royal Highness the Duke of Connaught was balloted for and elected a Fellow of the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "The Occurrence of Encystation in *Trypanosoma grayi* (Novy); with Remarks on Methods of Infection in Trypanosomes generally." By Professor E. A. MINCHIN. Communicated by Professor E. RAY LANKESTER, F.R.S.

II. "Note on the Continuous Rays observed in the Spark Spectra of Metalloids and some Metals." By Professor W. N. HARTLEY, F.R.S.

III. "The Composition of Thorianite, and the Relative Radio-activity of its Constituents." By Dr. E. H. BÜCHNER. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.

IV. "A Numerical Examination of the Optical Properties of Thin Metallic Plates." By Professor R. C. MACLAURIN. Communicated by Professor J. LARMOR, Sec. R.S.

V. "On a Compensated Micro-manometer." By B. J. P. ROBERTS. Communicated by Sir J. I. THORNYCROFT, F.R.S.

VI. "Experimental Investigation as to the Dependence of Gravity on Temperature." By L. SOUTHERNS. Communicated by Professor W. M. HICKS, F.R.S.

November 15, 1906.

Lord RAYLEIGH, O.M., D.C.L., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Professor J. Rose Bradford, Dr. A. E. H. Tutton, and Mr. W. Whitaker were elected Auditors of the Treasurer's Accounts on the part of the Society.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

The following papers were read:—

I. "Calcium as an Absorbent of Gases, and its Applications in the Production of High Vacua and for Spectroscopic Research." By F. SODDY. Communicated by Professor J. LARMOR, Sec. R.S.

II. "A Method of Gauging by Evaporation the Degree of High Vacua." (Addendum to Mr. F. Soddy's paper.) By A. J. BERRY. Communicated by Professor J. LARMOR, Sec. R.S.

III. "The Effect of Temperature on the Activity of Radium and its Transformation Products." By Dr. H. L. BRONSON. Communicated by Professor E. RUTHERFORD, F.R.S.

IV. "On the Refractive Indices of Gaseous Potassium, Zinc, Cadmium, Mercury, Arsenic, Selenium, and Tellurium." By C. CUTHBERTSON and E. P. METCALFE. Communicated by Professor F. T. TROUTON, F.R.S.

V. "The Photo-Electric Fatigue of Zinc." By H. S. ALLEN. Communicated by Professor H. A. WILSON, F.R.S.

November 22, 1906.

Sir LAUDER BRUNTON, Vice-President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the List of the Officers and Council for the ensuing year, proposed by the Council for election, was read as follows:—

President.—The Right Hon. the Lord Rayleigh, O.M., M.A., D.C.L.

Treasurer.—Alfred Bray Kempe, M.A.

Secretaries.—Professor Joseph Larmor, D.Sc., D.C.L., LL.D.; Sir Archibald Geikie, D.C.L., Sc.D., LL.D.

Foreign Secretary.—Francis Darwin, M.A., M.B.

Other Members of the Council.—The Right Hon. the Lord Avebury, D.C.L.; Sir Benjamin Baker, K.C.B.; Henry Frederick Baker, Sc.D.; Professor J. Norman Collie, Ph.D.; Professor Wyndham R. Dunstan, M.A.; Professor David Ferrier, M.D.; Professor Sydney J. Hickson,

D.Sc.; Sir William Huggins, K.C.B., O.M.; Professor Edwin Ray Lankester, M.A.; Hugh Frank Newall, M.A.; Alexander Scott, D.Sc.; Albert Charles Seward, M.A.; Professor William Johnson Sollas, Sc.D.; Professor Ernest Henry Starling, M.D.; Professor Silvanus Phillips Thompson, D.Sc.; Augustus Désiré Waller, M.D.

The following papers were read:—

I. "Studies on the Development of Larval Nephridia. Part II.—*Polygordius*." By Dr. CRESSWELL SHEARER. Communicated by A. SEDGWICK, F.R.S.

II. "The Structure of Nerve Fibres." By Professor J. S. MACDONALD. Communicated by Professor C. S. SHERRINGTON, F.R.S.

III. "On Opsonins in Relation to Red Blood Cells." By Dr. J. O. WAKELIN BARRATT. Communicated by Dr. C. J. MARTIN, F.R.S.

IV. "On the Inheritance of Certain Invisible Characters in Peas." By R. H. LOCK. Communicated by W. BATESON, F.R.S.

V. "The Influence of Increased Barometric Pressure on Man. No. 2." By LEONARD HILL, F.R.S., and M. G. GREENWOOD.

VI. "The Influence of the Kidneys on Metabolism." By Dr. F. A. BAINBRIDGE and Dr. A. P. BEDDARD. Communicated by Professor E. H. STARLING, F.R.S.

November 30, 1906.

ANNIVERSARY MEETING.

Mr. A. B. KEMPE, Treasurer, in the Chair.

The Report of the Auditors of the Treasurer's accounts was read, and the thanks of the Society were given to the Treasurer and to the Auditors.

The List of Fellows deceased and the List of Fellows elected into the Society since the last Anniversary were read.

The Report to the Society from the Council, upon the work during the past year, was, upon the motion of the Chairman, received.

The Treasurer read the Anniversary Address of the President, in his absence through illness.

On the motion of Sir John Murray, seconded by Admiral Sir H. B. Jackson, the thanks of the Society were voted to the President for his Address.

The Awards of the Medals for the year were announced as follows, and the Medals were presented from the Chair:—

The Copley Medal.....	To Prof. Elias Metchnikoff, For. Mem. R.S.
The Rumford Medal ...	„ Prof. H. L. Callendar, F.R.S.
A Royal Medal	„ Prof. A. G. Greenhill, F.R.S.
A Royal Medal	„ Dr. D. H. Scott, F.R.S.
The Davy Medal	„ Prof. Rudolf Fittig.
The Darwin Medal	„ Prof. Hugo de Vries, For. Mem. R.S.
The Hughes Medal	„ Mrs. W. E. Ayrton.

The Chairman having, with the consent of the Society, nominated Mr. Clement Reid and Professor H. H. Turner as Scrutators, to assist the Secretaries in examining the balloting lists for the election of Council and Officers, the votes of the Fellows present were taken. The Scrutators reported that the Council and Officers nominated at the preceding meeting had been duly elected, and their names were accordingly announced from the Chair.

The thanks of the Society were given to the Scrutators.

December 6, 1906.

Dr. FERRIER, Vice-President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Chairman announced that the President had appointed as Vice-Presidents—

The Treasurer.
Sir Benjamin Baker.
Dr. Ferrier.
Sir William Huggins.

The following Papers were read:—

I. "A Comparison of Values of the Magnetic Elements deduced from the British Magnetic Survey of 1891 with Recent Observation." By W. ELLIS, F.R.S.

II. "The Theory of the Compositions of Numbers.—Part II." By Major P. A. MACMAHON, F.R.S.

III. "On the Transpiration Current in Plants." By Professor H. H. DIXON. Communicated by Professor J. JOLY, F.R.S.

IV. "The Theory of Photographic Processes. Part III.—The Latent Image and its Destruction." By S. E. SHEPPARD and C. E. K. MEES. Communicated by Sir W. RAMSAY, K.C.B., F.R.S.

V. "The Chemistry of Globulin." By W. SUTHERLAND. Communicated by Dr. C. J. MARTIN, F.R.S.

December 13, 1906.

Sir WILLIAM HUGGINS, Vice-President, followed by the Treasurer, in the Chair.

His Royal Highness the Duke of Connaught (elected November 8) was admitted into the Society.

A List of the Presents received was laid on the table, and thanks ordered for them.

The following Papers were read:—

I. "The Relation between Breaking Stress and Extension in Tensile Tests of Steel." By A. MALLOCK, F.R.S.

II. "On the Intensity of Light Reflected from Transparent Substances." By Professor R. C. MACLAURIN. Communicated by Professor J. LARMOR, Sec. R.S.

III. "Contributions to our Knowledge of the Poison Plants of Western Australia. Part II.—*Oxylobium parviflorum*—Lobine." By E. A. MANN and Dr. W. H. INCE. Communicated by Professor J. N. COLLIE, F.R.S.

IV. "Experiments on the Length of the Cathode Dark Space with Varying Current Densities and Pressures in Different Gases." By F. W. ASTON. Communicated by Professor J. H. POYNTING, F.R.S.

V. "An Examination of the Lighter Constituents of Air." By J. E. COATES. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.

VI. "The Velocity of the Negative Ions in Flames." By E. GOLD. Communicated by Professor H. A. WILSON, F.R.S.

VII. "The Electric or Magnetic Polarisation of a Thin Cylinder of Finite Length by a Uniform Field of Force." By Dr. T. H. HAVELOCK. Communicated by Professor J. LARMOR, Sec. R.S.

VIII. "Further Observations on the Effects produced on Rats by the Trypanysomata of Gambia Fever and of Sleeping Sickness." By H. G. PLIMMER. Communicated by Dr. C. J. MARTIN, F.R.S.

The Society adjourned over the Christmas Recess to Thursday, January 17, 1907.

PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

A Note on the Theory of Directive Antennæ or Unsymmetrical Hertzian Oscillators.

By J. A. Fleming, M.A., D.Sc., F.R.S.

(Received March 15,—Read March 22,—Received in revised form May 24, 1906.)

The employment in wireless telegraphy of antennæ or radiating wires which have part of their length vertical and part horizontal, and possess the power of radiating unequally in various horizontal directions, draws attention to the particular qualities of bent electric oscillators when used as radiators or transmitters.* The object of the following note is to show that the properties of such radiators can be deduced from accepted principles, and that experimental results so far obtained are in general accordance with theory.

The nature of the field of electric and magnetic force round a short straight electric oscillator or doublet has been expressed analytically and delineated graphically in well-known memoirs by Hertz,† Pearson and Lee,‡ and others, and that around a not very short rod or linear oscillator has been

* See G. Marconi, LL.D., D.Sc., "On Methods whereby the Radiation of Electric Waves may be mainly confined to certain Directions, and whereby the Receptivity of a Receiver may be restricted to Electric Waves emanating from certain Directions," 'Roy. Soc. Proc.,' vol. 77, p. 413, 1906.

† H. Hertz, 'Wied. Ann.,' vol. 36, p. 1, 1889, or 'Electric Waves,' English translation, p. 137.

‡ Pearson and Lee, 'Phil. Trans.,' A, vol. 193, p. 159, 1900.

investigated by M. Abraham* and depicted by F. Hack.† In these cases we have perfect symmetry of radiation round the axis of the oscillator.

This equality is, however, destroyed by bending the oscillator, and it then radiates unequally in different directions taken in the equatorial or symmetrical plane of the oscillator through its centre, being somewhat greater or stronger on the convex side of the oscillator.

The analytical treatment of the subject presents, however, enormous difficulties unless we limit consideration to the case in which the current in the oscillator is assumed to have the same value at all points at the same time, and also that the dimensions of the oscillator are small compared with the distance from it of the points at which the field is considered.

One form of bent oscillator of the above kind may be considered to be made up by the superposition of three Hertzian electric doublets placed at right angles to each other, the poles being so arranged that at the two corners poles of opposite sign are superimposed, the oscillations in all being synchronous and similarly directed (see fig. 1). Hence, to obtain the field of the bent oscillator, we need merely to calculate those of the components and add them together.

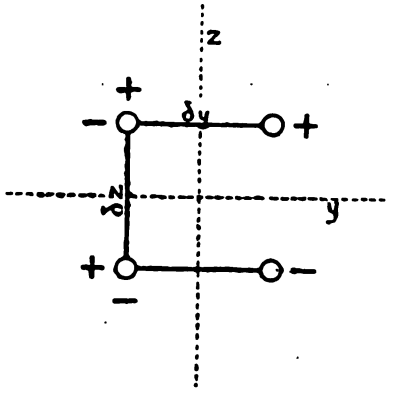

Fig. 1.

Let a single electric oscillator or doublet be placed with centre at the origin and axis coinciding with the z axis. Let oscillations exist in it of period $2\pi/n$, and radiation be emitted of wave-length $2\pi/m$. Suppose the length of the oscillator to be denoted by δz, the electric charge at either pole at any instant by q, the uniform current in the axis by i, whilst Q and I are the maximum values of q and i which vary so that $q = \mathrm{Q} \sin nt$ and $i = \mathrm{I} \cos nt$. Also let $\phi = \mathrm{Q}\delta z$ be the maximum electric moment of the

* M. Abraham, 'Ann. der Physik.,' vol. 66, p. 435, 1898.

† F. Hack, 'Ann. der Physik.,' vol. 14, p. 539, 1904.

oscillator. We have, therefore, $I = Qn$ or $\phi n = I\delta z$, and $n/m = v$, the velocity of propagation of the radiation through space. The scalar potential V at any point P whose distance from the origin is r is given by

$$V = -\frac{\phi}{k}\frac{d}{dz}\left(\frac{\sin(mr-nt)}{r}\right), \tag{1}$$

where k is the dielectric constant of the medium, and $r^2 = x^2+y^2+z^2$.

Also, if F, G, and H are the components of vector potential at P, we have in this case $F = G = 0$, and

$$H = -I\delta z\frac{\cos(mr-nt)}{r}. \tag{2}$$

If we employ the symbol Π to stand for $\sin(mr-nt)/r$, we can write the above expressions (1) and (2) in the form

$$V = -\frac{\phi}{k}\frac{d\Pi}{dz}, \qquad H = \phi\frac{d\Pi}{dt}. \tag{3}$$

If we suppose this doublet to be moved parallel to itself in the negative direction so that its centre is displaced by a distance $-\frac{1}{2}\delta y$, the scalar and vector potentials at P become—

$$V = \left(-\frac{\phi}{k}\frac{d\Pi}{dz}\right)+\tfrac{1}{2}\frac{d}{dy}\left(\frac{\phi}{k}\frac{d\Pi}{dz}\right)\delta y, \tag{4}$$

$$H = \phi\frac{d\Pi}{dt}-\tfrac{1}{2}\frac{d}{dy}\left(\phi\frac{d\Pi}{dt}\right)\delta y. \tag{5}$$

Consider, then, two other similar doublets of length δy, and maximum moment ϕ', placed with poles pointing in opposite directions and axes parallel to the axis of y, the doublets having centres at distances $+\frac{1}{2}\delta z$ and $-\frac{1}{2}\delta z$ from the origin and poles arranged as in fig. 1. The scalar and vector potentials at the point P of these last two doublets constituting together a double-doublet are obviously given by—

$$V = -\frac{\phi'}{k}\frac{d^2\Pi}{dz\,dy}\delta z, \tag{6}$$

$$G = \phi'\frac{d^2\Pi}{dz\,dt}\delta z. \tag{7}$$

Hence, if three such short, straight oscillators, having equal currents and charges, are placed round the origin so as to create a doubly-bent oscillator, the scalar and vector potentials of this oscillator at a point P (see fig. 2), the distance of which from the origin is large compared with the linear dimensions of the oscillator, are given by—

$$V = -\frac{\phi}{k}\frac{d\Pi}{dz}+\tfrac{1}{2}\frac{\phi}{k}\frac{d^2\Pi}{dy\,dz}\delta y-\frac{\phi'}{k}\frac{d^2\Pi}{dz\,dy}\delta z. \tag{8}$$

$$\left.\begin{aligned} F &= 0, \\ G' &= \phi' \frac{d^2\Pi}{dz\,dt}\delta z, \\ H &= \phi \frac{d\Pi}{dt} - \tfrac{1}{2}\phi \frac{d^2\Pi}{dy\,dt}\delta y, \end{aligned}\right\} \qquad (9)$$

where $\phi'\delta z = \phi\delta y$.

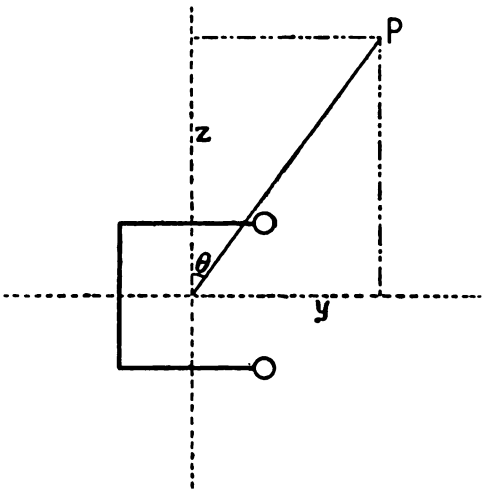

FIG. 2.

The electric and magnetic forces at the point P, of which the axial components are P, Q, R, and a, b, c, can be obtained from equations (8) and (9) at once by the aid of the relations—

$$\left.\begin{aligned} P &= -\frac{dF}{dt} - \frac{dV}{dx}, & a &= \frac{dH}{dy} - \frac{dG}{dz}, \\ Q &= -\frac{dG}{dt} - \frac{dV}{dy}, & b &= \frac{dF}{dz} - \frac{dH}{dx}, \\ R &= -\frac{dH}{dt} - \frac{dV}{dz}, & c &= \frac{dG}{dx} - \frac{dF}{dy}, \end{aligned}\right\} \qquad (10)$$

It is obvious that if the electric circuit is completed by placing a pair of double-doublets of moments ϕ and ϕ' at right angles to each other with poles directed in like sense all round the origin, the free charges cancel each other pair and pair, and we are left with a closed electric circuit of area $\delta y \,.\, \delta z$, traversed by a maximum current I. This quadruple doublet creates potentials such that

$$\left.\begin{aligned} V &= 0, & F &= 0, \\ G &= \phi' \frac{d^2\Pi}{dz\,dt}\delta z, & H &= \phi \frac{d^2\Pi}{dy\,dt}\delta y, \end{aligned}\right\} \qquad (11)$$

where $\phi'\delta z = \phi\delta y$.

Such a completely closed circuit or *magnetic doublet* creates, therefore, periodic electric and magnetic forces in its field when current oscillations are set up in the circuit.*

For the present purposes we require only the electric and magnetic forces perpendicular to the radius vector r, taken at its extremity, when that radius is taken in the plane xy, which is normal to the plane yz in which the oscillator is situated. Hence we need only calculate the value of R, a, and b for the case in question.

If we write M for $I\,\delta y\,\delta z$ and call this the magnetic moment of the bent oscillator, so that $\phi\delta y = \phi'\delta z = M/n$, we have the following equations for the potentials and forces in the field at points not very near the oscillator—

$$\begin{aligned}
V &= -\frac{\phi}{k}\frac{d\Pi}{dz} + \frac{\phi}{2k}\frac{d^2\Pi}{dy\,dz}\delta y - \frac{\phi'}{k}\frac{d^2\Pi}{dz\,dy}\delta z = -\frac{\phi}{k}\frac{d\Pi}{dz} - \frac{M}{2kn}\frac{d\Pi}{dy\,dz},\\
G &= \phi'\frac{d^2\Pi}{dz\,dt}\delta z = \frac{M}{n}\frac{d^2\Pi}{dy\,dt},\\
H &= \phi\frac{d\Pi}{dt} - \frac{\phi}{2}\frac{d^2\Pi}{dy\,dt^2}\delta y = \phi\frac{d\Pi}{dt} - \frac{M}{2n}\frac{d^2\Pi}{dy\,dt},\\
R &= -\phi\frac{d^2\Pi}{dt^2} + \frac{M}{2n}\frac{d^3\Pi}{dy\,dt^2} + \frac{\phi}{k}\frac{d^2\Pi}{dz^2} + \frac{M}{2kn}\frac{d^3\Pi}{dy\,dz^2},\\
a &= \phi\frac{d^2\Pi}{dy\,dt} - \frac{M}{2n}\frac{d^3\Pi}{dy^2\,dt} - \frac{M}{n}\frac{d^3\Pi}{dz^2\,dt},\\
b &= -\phi\frac{d^2\Pi}{dx\,dt} + \frac{M}{2n}\frac{d^3\Pi}{dx\,dy\,dt}.
\end{aligned} \tag{12}$$

Performing the necessary differentiations on the function $\Pi = \sin(mr-nt)/r$ and collecting terms in $\sin(mr-nt)$ and $\cos(mr-nt)$, which for shortness will be written $\sin X$ and $\cos X$, also putting v for n/m or $(\mu k)^{-\frac{1}{2}}$, where μ and k are the permeability and dielectric constant of the medium, we have the following expressions for R, a, and b.

* In the discussion on Mr. Marconi's paper (*loc. cit.*), read at the Royal Society on March 22, 1906, Professor J. Larmor, Sec. R.S., pointed out that the bent antenna employed by Mr. Marconi was equivalent in effect at distant points to the combination of a magnetic doublet or bi-pole magnetic oscillator of the kind investigated, in advance of Hertz's discovery of electric radiation, by Professor G. F. Fitzgerald (see 'The Scientific Writings of the late Professor G. F. Fitzgerald,' edited by Professor J. Larmor, p. 128), and a straight Hertzian doublet or bi-pole electric oscillator. It is obvious that if a straight electric oscillator is placed in contiguity to one side of a closed rectangular circuit or magnetic oscillator, the currents being of the same value and directed in an opposite sense in the open and adjacent side of the closed circuit, the resultant electromagnetic effect must be that of a doubly bent oscillator of the type considered in the text. The equations (8), (9), (4), (5), and (11) are consistent with this mode of viewing the facts.

$$R = \left\{\phi(m^2r^2-1)-\phi(m^2r^2-3)\left(\frac{z}{r}\right)^2+\frac{M}{2v}\frac{3}{mr}\left(\frac{y}{r}\right)\right.$$
$$\left.+\frac{M}{2v}\frac{(8m^2r^2-15)}{mr}\left(\frac{y}{r}\right)\left(\frac{z}{r}\right)^2\right\}\frac{\sin X}{kr^3}$$
$$+\left\{\phi mr-\phi 3mr\left(\frac{z}{r}\right)^2-\frac{M}{2v}(m^2r^2+3)\left(\frac{y}{r}\right)+\frac{M}{2v}(m^2r^2+18)\left(\frac{y}{r}\right)\left(\frac{z}{r}\right)^2\right\}\frac{\cos X}{kr^3}. \quad (13)$$

$$a = \left\{\phi vm^2r^2\left(\frac{y}{r}\right)+\frac{M}{2}3mr\left(\frac{y}{r}\right)^2-\frac{M}{2}3mr+3Mmr\left(\frac{z}{r}\right)^2\right\}\frac{\sin X}{r^3}$$
$$+\left\{\phi vmr\left(\frac{y}{r}\right)-\frac{M}{2}(m^2r^2-3)\left(\frac{y}{r}\right)^2-\frac{3M}{2}-M(m^2r^2-3)\left(\frac{z}{r}\right)^2\right\}\frac{\cos X}{r^3}. \quad (14)$$

$$b = -\left\{\phi vm^2r^2\left(\frac{x}{r}\right)+\frac{M}{2}3mr\left(\frac{x}{r}\right)\left(\frac{y}{r}\right)\right\}\frac{\sin X}{r^3}$$
$$-\left\{\phi vmr\left(\frac{x}{r}\right)-\frac{M}{2}(m^2r^2-3)\left(\frac{x}{r}\right)\left(\frac{y}{r}\right)\right\}\frac{\cos X}{r^3}. \quad (15)$$

Suppose we limit attention to the value of the electric force e and the magnetic force d at right angles to the extremity of the radius vector r, the former being parallel to the z-axis and the latter being drawn in the plane of xy. The magnetic force d in this direction is equal to $ay/r-bx/r$. Hence we obtain its value by multiplication of the values of a and b by y/r and x/r and subtraction. Then putting $z=0$ in the above equations and writing $\cos\theta$ for y/r we have,

$$e = \left\{\phi(m^2r^2-1)+\frac{M}{2v}\frac{3}{mr}\cos\theta\right\}\frac{\sin X}{kr^3}+\left\{\phi mr-\frac{M}{2v}(m^2r^2+3)\cos\theta\right\}\frac{\cos X}{kr^3}, \quad (16)$$

$$d = \{\phi vm^2r^2\}\frac{\sin X}{r^3}+\left\{\phi vmr-\frac{M}{2}m^2r^2\cos\theta\right\}\frac{\cos X}{r^3}. \quad (17)$$

If we denote the amplitudes of e and d by E and H, we have finally

$$E = \frac{1}{kr^3}\left[\left\{\phi(m^2r^2-1)+\tfrac{3}{2}\frac{M}{v}\frac{\cos\theta}{mr}\right\}^2+\left\{\phi mr-\frac{M}{2v}(m^2r^2+3)\cos\theta\right\}^2\right]^{\frac{1}{2}}, \quad (18)$$

$$H = \frac{1}{r^3}\left[(\phi vm^2r^2)^2+\left(\phi vmr-\frac{M}{2}m^2r^2\cos\theta\right)^2\right]^{\frac{1}{2}}, \quad (19)$$

where E is the amplitude of the electric force perpendicular to the radius vector and to the equatorial plane, and H is the amplitude of the magnetic force perpendicular to the radius vector and in the equatorial plane.

Hence, since m^2r^2 is always much greater than $1/mr$, it is clear that when θ is 180° the values of E and H are both greater than when $\theta = 0°$.

If we put $M = 0$ in the above equations they reduce to the values given by Hertz for the electric and magnetic forces of the short straight oscillator or doublet taken in the equatorial plane, the electric force being parallel to the axis and magnetic force at right angles. When mr is large compared with unity we have $kE^2 = \mu H^2$, showing that the energies of the magnetic and electric components of the wave then become equal. Also there is a minimum value of H and E corresponding to a value of θ, such that

$$\cos\theta = \frac{2\phi v}{M}\frac{1}{mr}, \quad \text{or} \quad \cos\theta = \frac{2\phi v}{M}\frac{mr}{m^2r^2+3}. \tag{20}$$

The above expressions are numerically small when r is large compared with the wave-length of the radiation. Hence a minimum value of the forces at the extremity of the radius vector is found, corresponding to some azimuthal angle θ rather less than 90° reckoned from the direction in which the free ends of the bent oscillator point.

A reference to the records of observations made by Mr. Marconi* on the radiation from a bent antenna shows that the above deductions from theory agree with his observed facts. Hence we conclude that whereas a straight vertical oscillator earthed at the lower end radiates equally in all horizontal directions or azimuths, the result of bending the antenna over to one side, so that a portion of it is horizontal, is to cause it to radiate less vigorously in the direction in which the free end points than in the opposite direction, and to create a minimum radiation in two other directions equally inclined to the direction of maximum radiation.

The degree of this fore-and-aft inequality in the plane of the oscillator will depend upon the ratio of the magnitude of the quantities $\frac{1}{2}Mmr$ and ϕv, or upon the ratio of δy to $2/m^2r$, that is upon the ratio of

$$\frac{\delta y}{\frac{1}{2}\delta z + \delta y} \quad \text{to} \quad \frac{4}{m^2rl}, \quad \textit{i.e.}, \text{ to} \quad \frac{\lambda^2}{\pi^2 rl},$$

where $2l$ is the total length of the bent oscillator. The greatest inequality between the fore and aft radiation in the plane of the oscillator will exist when π^2 times the ratio of the sum of the lengths of the two horizontal parts of the oscillator to its total length is as nearly as possible equal to the product of the ratios of λ^2/l^2 and l/r. The ratio λ/l is fixed by the geometrical form of the oscillator, hence the inequality in radiative power in the fore and aft directions for a given oscillator essentially depends upon the ratio of wave-length to the distance of the point at which observations are made, and at large distances will only be sensible when long wave-

* See 'Roy. Soc. Proc.,' A, vol. 77, p. 415, 1906.

lengths are employed. This result also agrees with the observations of Mr. Marconi, who says* :—

"I have observed that, in order that the effects should be well marked, it is necessary that the length of the horizontal conductors should be great in proportion to their height above the ground, and that the wave-lengths employed should be considerable, a condition which makes it difficult to carry out such experiments within the walls of a laboratory.

"I have found the results to be well marked for wave-lengths of 150 metres and over, but have not been able to obtain as well-defined results when employing much shorter waves, the effects following some law which I have not yet had time to investigate."

The above theoretical examination of this operation of a bent oscillator shows clearly that its unsymmetrical radiation in the equatorial plane depends not upon absolute wave-length, but upon the ratio of wave-length to the distance of the receiving point and upon the proportion between the length of the vertical and of the horizontal portions of the oscillator.

The theory is thus supported by the observed facts. If necessary, it would be possible from the equations given above to delineate the lines of electric force in the field of the bent oscillator for various epochs. Thus if R and Q are the components of the electric force in the plane yz, the differential equation to the lines of electric force in that plane is $Rdy - Qdz = 0$. The substitution of the values of R and Q and integration of this equation would furnish the equation to the lines of electric force in the yz plane from which they might be delineated, but its complexity does not make the task of actually delineating the lines of force for the bent oscillator an inviting one.

* *Loc. cit.*, p. 420.

The Law of Distribution in the Case in which one of the Phases possesses Mechanical Rigidity: Adsorption and Occlusion.

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Introduction.

The term "occlusion" has been applied somewhat indiscriminately to denote the state in which a gas exists in a solid, by which it has been absorbed, or from which it is evolved on heating, and no doubt the term includes phenomena of a totally different character. Similarly, the term "adsorption" is commonly used to differentiate between simple cases of solution and the removal of substances from solutions by solids in contact with them. It is the object of this paper to point out similarities which exist between certain cases, which may be included in these two groups, and to make some suggestions as to the classification of the phenomena.

In the first place we may dispose of certain instances in which solids evolve gases when they are heated, the change being irreversible. In 1898* I succeeded in showing that the evolution of such gases as hydrogen and carbon monoxide from minerals on heating did not require the assumption of their previous existence in the minerals at all; hence, there was no need to introduce the term occlusion to explain it. I proved that the gases were produced by the interaction of water vapour and carbon dioxide with such substances as ferrous oxide, the change being followed quantitatively. Later,† I put forward an explanation of the evolution of helium from minerals, in which it cannot be supposed to be present in a state of chemical combination. Ramsay and Soddy had shown that helium was one of the products of radio-active change, and had suggested that its presence in the minerals was due to the decay of some radio-active substance which they had formerly contained. This explanation did not, however, account for the retention of the gas in the mineral, and the clue to the solution of this part of the problem was given by Jaquerod's discovery‡ that helium would pass through the walls of a quartz bulb at a comparatively low temperature, though this material is quite impermeable to it in the cold. It follows that the gas may be present in the mineral in a state of supersaturation, and may

* 'Roy. Soc. Proc.,' vol. 64, p. 131.

† 'Nature,' January, 1905.

‡ 'Comptes Rendus,' 1904, vol. 139, p. 261.

remain in that state for an indefinite time, if the temperature is moderately low. When, however, the mineral is heated, the gas can diffuse freely through it, and there is a tendency to establish equilibrium between the two phases.

Many cases in which solids, or at least substances which are apparently solids, absorb and evolve gases reversibly have been investigated, and the experimental data are, in some of them, sufficient for the purpose of comparison. However, I only intend to consider the absorption of gases by palladium, platinum, and carbon, and as in the last case the measurements of the pressure-concentration relationships for small concentrations did not seem to be of sufficient accuracy, or to cover a sufficiently wide range of temperature, for my purpose, I have made some measurements of the quantity of hydrogen and carbon dioxide absorbed by carbon, between 100° C. and — 190° C., and at pressures up to one atmosphere, for myself. I shall refer to the work of others as I come to discuss it, but I can state here that Dewar's demonstration of the very complete absorption of gases by carbon at low temperatures made it clear that the results obtainable with this substance would prove of high interest.*

Experimental Part—The Apparatus.

The apparatus (fig. 1) employed in this investigation was very similar to the gas thermometer, described in the paper by Senter, Jaquerod, and myself,† on the vapour pressures of liquid hydrogen and liquid oxygen. As, however, it was considerably modified for this purpose I shall be obliged to give a brief description of it. The carbon was contained in the bulb *a*, which was about 1·5 cm. in diameter, and 2·5 cm. long. For convenience in filling it with carbon, the part *b* of the stem for the first centimetre next to it was about 0·3 cm. in diameter. After the carbon had been introduced, and covered with a plug of asbestos to prevent it from rising into the capillary stem *c*, the latter was sealed to it.

* The first quantitative investigation of the absorption of gases by charcoal appears to have been carried out by Th. de Saussure (Gilbert's 'Annalen der Physik,' 1814, vol. 47, p. 112; Thomson's 'Annals of Philosophy,' 1815, vol. 6, p. 241). He showed that Henry's law, which he verified by means of his apparatus, did not apply to this phenomenon. His values for the relationships between the pressure and the volume of oxygen absorbed at about 65° F. are fairly well reproduced by the expression we have been considering. Thus—

p (inches of mercury).	v.	$\sqrt[4]{p}/v$.
28·91	34·5	0·068
15·90	27·5	0·072
10·26	24·5	0·072

† 'Phil. Trans.,' A, vol. 200, p. 142.

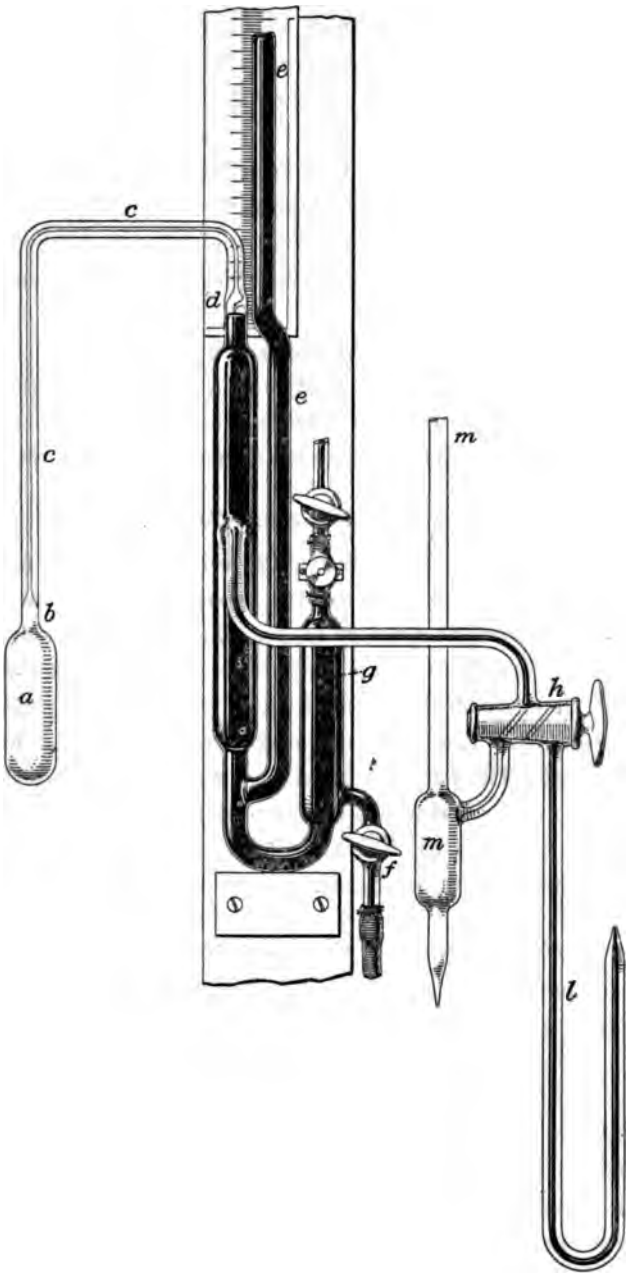

FIG. 1.

The tube which formed the dead-space *d* was calibrated before it was sealed to the rest of the apparatus. The volume of the space above the surface of the mercury, when the latter was in contact with the point,

was determined, and also the volume of 1 mm. of the tube below it; so that if the distance of the surface of the mercury from the point was known, the volume of the space above could be calculated.

The pressure exerted by the gas in the apparatus was measured by bringing the mercury in *d* close to the point, and observing the height to which the column rose in the barometer tube *e*. The volume of mercury in the apparatus was adjusted by means of a reservoir connected through a rubber tube and stop-cock at *f*; bubbles of air were caught in the tube *g*.

The gas was introduced, and the apparatus exhausted, through a stop-cock *h*, to which were connected a syphon *l*, for drawing the gas out of tubes in which it was contained over mercury, and a tube *m*, leading through an arrangement for catching drops of mercury to the pump.

The Preparation of the Carbon.

The carbon was prepared by calcining the soft part of the cocoanut, at a temperature not above a dull red heat, till vapour ceased to be evolved, and then cooling the product as quickly as possible. After it had been introduced into the bulb, and the latter sealed to the stem and dead-space, it was heated to 440° C. *in vacuo* for some hours, by surrounding the bulb with a bath of sulphur vapour, and maintaining a *vacuum* in the apparatus by means of the pump. The mass of the carbon was determined at the end of the experiments by transferring the contents of the bulb to a closely-covered platinum crucible, drying it at 150° C., weighing, and afterwards determining the loss of weight on combustion in air.

The Preparation and Method of Measurement of the Gases.

Intending to investigate the absorption of a number of gases by carbon, I selected, as two extreme cases, hydrogen and carbon dioxide, for the first experiments. Soon after I commenced my work, however, I heard from Sir W. Ramsay that he and Miss I. Homfray, B.Sc., were engaged on a similar research, so I decided to limit my own investigation to the two gases mentioned above. In either case the gas was obtained from a Kipp's apparatus, which had been in use so long that the gas delivered from it might be considered to be free from air. The gases were dried by passing through tubes containing pentoxide of phosphorus, and were collected in tubes over mercury.

Successive volumes of gas, each of about 5 c.c., were delivered into the apparatus, and after the addition of each quantity, a series of measurements of the p, v, t, relationships was made. These quantities of gas were measured

in a constant-pressure gas-burette, such as I have described in "The Experimental Study of Gases" (p. 67). The temperature of the water and the height of the barometer were observed simultaneously. In the whole of the calculations involved in this research the coefficient of expansion of carbon dioxide is taken to be 1/273·5 and that of hydrogen to be 1/273; it has also been assumed that, within the limits of the pressures investigated, the product pv could be taken as constant.

The Method of Calculating the Results.

To obtain the relationship between the pressure exerted by the gas in the apparatus and its concentration in the carbon, it was necessary to obtain the following data:—

(*a*) The mass of the carbon: this amounted to 1·400 grammes, and was associated with 0·095 gramme of ash.

(*b*) The mass of gas introduced into the apparatus, a factor which could be deduced directly from the burette readings, the temperature, the pressure, and the density of the gas.

(*c*) The volume of the dead-space, and of that portion of the stem which remained at the air temperature. This is given by the formula $v\,\mathrm{ds} = 1{\cdot}36 + 0{\cdot}060h$, where h is the distance of the surface of the mercury from the point.

(*d*) The volume of the bulb, and of that part of the stem which was at the same temperature, was determined by an indirect method. Two successive quantities of hydrogen, previously measured in the burette, were introduced into the apparatus, and while both bulb and dead-space were at the air temperature, the pressure and the temperature were carefully observed. Now from the formula:—

$$\frac{pv}{t} = \frac{p'(v\,\mathrm{ds} + v\,\mathrm{bulb})}{t'},$$

where p, v, t are the pressure, volume, and temperature of the hydrogen in the burette, and p' and t' are the pressure and temperature in the apparatus, it is possible to calculate the volume of the gas in the bulb. Thus:—

p.	v.	t.	p'.	t'.	v ds.	v bulb.
737·3	3·38	8°·2 C.	418·3	16°·0 C.	1·41	4·72
738·2	5·64	8°·4 C.	683·0	15°·7 C.	1·41	4·86

The result shows that at the higher pressure the bulb contains more hydrogen than at the lower pressure, as of course it should do, since the gas is slightly soluble in the carbon. However, as we shall see

later, it is probable that at this temperature the amount absorbed can be taken as proportional to the pressure, so that we can calculate the true volume of the free space in the bulb, which works out at 4·52 c.c.

The formula given above may be used to calculate the quantity of gas in the bulb, which must be subtracted from the quantity introduced into the apparatus in order to calculate the quantity absorbed by the carbon; it then takes the form:—

$$\frac{pv}{t} = p\left\{\frac{v\,\text{bulb}}{t'} + \frac{v\,\text{ds}}{t''}\right\},$$

where t' and t'' are the temperature of the bulb and dead-space respectively.

As a matter of fact, no correction was made for the change of volume of the bulb, for the expansion of the carbon, or for the volume of the condensed gas. So long as the pressures remained low and the correction, which is the product on the left-hand side of the equation, small, this could have but little effect upon the result, but it might obviously vitiate results dependent on the measurement of higher pressures, and which, as will appear presently, must be very exact, if they are to be of any value at all.

The Method of Conducting the Experiments.

The object of each experiment was to determine the relationship between the pressure and the quantity of gas absorbed at a particular temperature. The temperatures at which experiments were made corresponded to 100°, 35°, 61°, 0°, −78°, and, in the case of hydrogen, to about −190°. The first three temperatures were obtained by boiling water, chloroform, and ether, respectively, in a vapour jacket surrounding the bulb. Barometric corrections were not applied, as the small variation of temperature with pressure did not materially affect the results, and to apply corrections would have entailed a great deal more experimental work. The ice-point was of course obtained by immersing the bulb in melting ice. A mixture of solid carbon dioxide and alcohol in a vacuum vessel will, if the latter is well exhausted, remain at −78° for some hours; and liquid air, contained in a two-litre globular vacuum vessel, will only be reduced to about half its volume in three days, and the temperature will not have risen more than 3°.

The time which elapsed before equilibrium was established varied considerably under different conditions. In the case of the absorption of hydrogen by carbon at the temperature of liquid air it was often some hours before the column of mercury came to rest. In the case of carbon dioxide equilibrium was always most rapidly established at the lower tempera-

tures. Thus, working at −78°, the bulb of the apparatus was allowed to remain in the bath of solid carbon dioxide and alcohol for about three hours (p. 16, Experiment *u*), when it was noticed that the pressure did not vary after the first few minutes of the experiment. After reading the pressure the bath was removed, and when the bulb had regained the temperature of the air it was again cooled. In a few minutes the pressure was identical with that observed at the first reading. At 100° equilibrium was more slowly established, the pressure appearing to rise at first and then to fall slowly. So as to eliminate errors arising from such a source, the bulb was usually allowed to remain at the temperature of the vapour for at least three hours, or, in fact, till equilibrium appeared to be established.

Experiments with Carbon Dioxide.

The following experiments were carried out in the manner described above, and form one continuous series, successive quantities of the gas being added after each set of measurements at the four temperatures. The results are plotted on the accompanying diagram, and it may be said that there is at least some internal evidence that they are satisfactory.

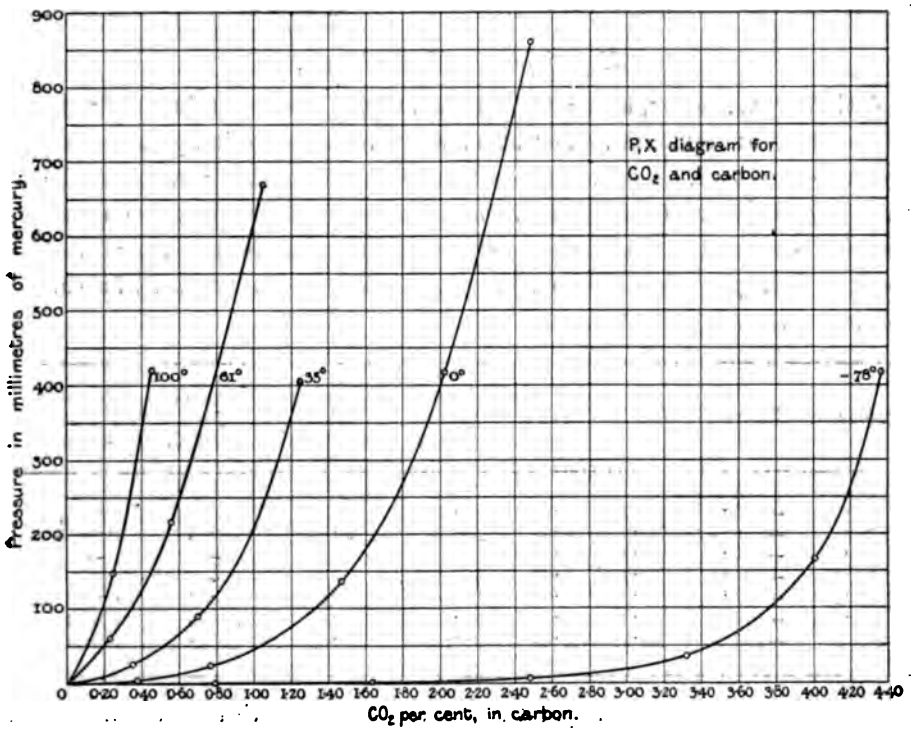

FIG. 2.

The mass of carbon contained in the bulb was, as has already been stated, 1400 grammes; the volume of the bulb and of the dead-space have been given on p. 13.

	P.(corr.).	T. bulb.	T. d. s.	V. d. s.	Volume of gas in apparatus.	Volume of gas unabsorbed.	Volume of gas absorbed.	CO_2 per cent. by weight.
	mm.	C.	C.		c.c.	c.c.	c.c.	
(*a*) ...	4·1	0°	11·0°	1·39	2·75	0·03	2·72	0·38
(*b*) ...	26·8	35	15·5	1·45	—	0·18	2·57	0·36
(*c*) ...	62·2	61	14·0	1·37	—	0·39	2·36	0·33
(*d*) ...	148·3	100	18·0	1·54	—	0·98	1·77	0·25
(*e*) ...	0·2	−78·2	15·0	1·40	5·72	0	5·72	0·795
(*f*) ...	25·1	0	15·5	1·97	—	0·21	5·51	0·77
(*g*) ...	89·5	35	15·5	1·81	—	0·67	5·05	0·70
(*h*) ...	215·0	61	14·5	1·54	—	1·72	4·00	0·56
(*l*) ...	420·0	100	16·0	1·48	—	2·60	3·12	0·435
(*m*) ...	1·4	−78·2	18·0	1·42	11·83	0·01	11·82	1·63
(*n*) ...	137·4	0	15·7	1·74	—	1·12	10·71	1·47
(*o*) ...	406·8	35	18·0	1·42	—	2·85	9·02	1·25
(*p*) ...	668·2	61	19·0	1·40	—	4·42	7·41	1·03
(*r*) ...	416·4	0	15·5	1·96	18·18	3·50	14·68	2·02
(*s*) ...	6·2	−78·2	15·0	1·48	—	0·07	18·11	2·48
(*t*) ...	858·6	0	14·0	1·57	24·83	6·67	18·16	2·485
(*u*) ...	35·2	−78·2	12·2	1·60	—	0·36	24·47	3·32
(*v*) ...	165·4	−78·2	16·0	1·45	31·39	1·65	29·74	4·01
(*w*) ...	418·4	−78·2	16·5	1·94	37·69	5·13	32·56	4·37

Experiments with Hydrogen.

A similar set of experiments was made with hydrogen, but only at the temperature of liquid air. For at higher temperatures it appears that the pressure-concentration curve is nearly linear, and results would only be of value if they were of a sufficiently accurate character to enable one to distinguish between the linear relationship and slight deviations from it. The results when plotted give a curve very similar to that obtained for carbon dioxide at the ice-point.

P. (corr.).	T. bulb.	T. d. s.	V. d. s.	Volume of gas in apparatus.	Volume of gas unabsorbed.	Volume of gas absorbed.	Hydrogen per cent. by weight.
mm.	C.	C.		c.c.	c.c.	c.c.	
3·1	−192·0°	15·0°	1·50	5·32	0·07	5·25	0·0335
12·1	−192·5	14·0	1·37	10·49	0·26	10·23	0·0655
14·0	−191·0	16·0	1·37	—	—	—	—
14·2	−191·0	16·0	1·60	—	—	—	—
51·7	−190·0	15·0	1·37	17·16	1·13	16·03	0·103
134·5	−190·0	20·0	2·31	23·57	3·02	20·55	0·132
248·0	−189·0	14·5	2·64	29·12	5·67	23·45	0·150

In each experiment the apparatus was left at rest with the bulb immersed in liquid air for 24 hours before a reading was taken, and it will be observed

that, even with this precaution, the results are not so satisfactory as those obtained in the case of carbon dioxide. The slight irregularities which occur at 12 to 14 mm. cannot be attributed to the inconstancy of the temperature.

Discussion of the Results.

On examining the results, one is at once struck by the similarity between the pressure-concentration curves for the gases hydrogen and carbon dioxide in solution in carbon and those which have been obtained by Hoitsema* and by Ramsay, Mond, and Shields,† for the absorption of gases by palladium and platinum. The curves are in each case represented by the formula

$$\sqrt[n]{p}/x = \text{constant},$$

where p is the pressure of the gas corresponding to the concentration x in the "solid" phase, and n increases as the temperature falls. Thus we have for carbon dioxide

Temperature.	p.	x.	$\sqrt[2]{p}/x$.	$\sqrt[3]{p}/x$.
100° C.....	148·3	0·25	21·2	48·7
	420·0	0·435	17·2	47·1
61° C.....	62·2	0·33	12·0	23·9
	215·0	0·56	10·7	26·4
	668·2	1·03	8·5	25·2
35° C.....	26·8	0·36	8·3	14·4
	89·5	0·70	6·4	13·5
	406·8	1·25	5·9	16·1
0° C.....	4·1	0·38	4·1	
	25·1	0·77	3·8	
	137·4	1·45	3·8	
	416·4	2·02	3·7	
	858·6	2·48	3·8	

The formula does not apply so well to the pressure-concentration curve for −78° C., but a fair approximation is obtained by calculating the values of $\sqrt[3]{p}/x$.

It would appear, then, that n is almost exactly equal to 3 for the isothermal at 0° C., and to 2 for the isothermal at 100° C. It follows that at higher temperatures it probably reaches the limiting value, unity, when carbon dioxide will dissolve in carbon in strict accordance with the law of distribution.

If we apply the same method to the results obtained with hydrogen,

* 'Zeit. Phys. Chem.,' 1895, vol. 17, p. 1.

† 'Phil. Trans.,' vol. 186, p. 657; vol. 190, p. 120; vol. 191, p. 105.

we find that this gas at −190° C. behaves similarly to carbon dioxide at 0° C.

Temperature.	p.	x.	$\sqrt[3]{p}/x$.	$\sqrt[3]{p}/x$.
−190° C.	3·1	0·0335	52·6	43·5
	14·0	0·0655	57·0	36·8
	51·7	0·103	70·0	36·2
	134·5	0·132	88·0	38·8
	248·0	0·150	106·0	42·4

Hoitsema* investigated the pressure-concentration relationships for hydrogen and palladium, at temperatures between 0° and 250° C. The curve he obtained for the isothermal 0° C. is similar to that for carbon dioxide and carbon at −78° C., and the isothermal for 30° C. is not to be distinguished from it at low pressures. The isothermal for 100° C., and those at higher temperatures, consist of three portions; that corresponding to low pressures, at which, as in the case of carbon dioxide and carbon, p increases more rapidly than x; a horizontal portion, where x increases without increase in p, corresponding to the condensation of a gas; and a portion which is nearly perpendicular, where x hardly increases at all with increase of p. It is the first portion, corresponding to small concentration, which is of interest to us at the moment.

Hoitsema points out that this portion of the curve is represented by the same formula which we have found to represent the pressure-concentration curves for carbon dioxide and carbon, though he states his results in terms of the volume occupied by two milligrammes of hydrogen. The following table contains a summary of his results:—

Temperature.	p.	v.	pv.	$pv/\sqrt[3]{p}$.
100° C.....	12·2	2·903	35·4	10·1
	93·1	1·050	97·7	10·1
150° C.....	26·2	3·084	80·8	15·8
	165·4	1·299	214·8	16·6
	393·7	0·771	303·5	15·3
200° C.....	41·7	3·524	146·9	22·6
	116·4	2·146	249·3	23·1
	218·2	1·542	366·4	22·7
	484·0	0·987	477·7	21·7
	752·3	0·695	522·8	19·1
	1822·6	0·366	667·1	15·6

It will be observed that while $pv/\sqrt[3]{p}$ is constant for the values obtained for p and v at 100° C. over the whole range investigated, and for com-

* *Loc. cit.*

paratively low pressures at higher temperatures, there is a tendency under the latter conditions for the product pv to attain a more constant value, particularly at the higher pressures.

Hoitsema suggests that his results indicate that hydrogen, in solution in palladium, is dissociated into single atoms, but that as the concentration increases association takes place, and the solution contains complexes of the formula H_2. This hypothesis finds support in Nernst's investigation* of the distribution of such substances as benzoic acid between water, in which it appears to exist as simple molecules, and benzene, in which it appears to exist as complexes of the formula $(C_6H_6)_2$. It appears, however, that this is highly improbable, for, if it were so, it would necessarily follow that this gas, dissolved in amorphous carbon at $-190°$ C., must be supposed to be dissociated into fractions of an atom.

Mond, Ramsay, and Shields† investigated the absorption of oxygen by palladium and came to the conclusion that the gas was absorbed with the formation of a mixture of oxides. The substance formed appears to be a brown powder, totally different from palladium, and no oxygen could be removed from it at a red heat. They considered that if it were possible to leave the metal long enough in contact with oxygen it would be completely converted into the oxide, PdO. Thermochemical measurements supported this view.

They also investigated the absorption of hydrogen by platinum, and though their work deals chiefly with the effect of temperature on the evolution of hydrogen from the metal, they determined the pressure-concentration relationships for pressures up to 767 mm. at 18° C. The curve representing their results is very similar to the pressure-concentration curve for carbon dioxide and carbon at $-78°$ C. or for palladium and hydrogen at 0° C.; 13 c.c. of gas were absorbed before any rise in pressure was observed, the curve rising at first slowly and then rapidly. It appears then that these three cases present marked similarities.

Discussion of the Results.

Schmidt‡ has shown that when animal charcoal absorbs iodine from solution the distribution of the solute between the solid and liquid phases is given by the formula

$$(x \text{ solid})^4/(x \text{ solution}) = \text{constant},$$

* 'Zeit. Phys. Chem.,' 1891, vol. 8, p. 110.

† *Loc. cit.*

‡ 'Zeit. Phys. Chem.,' vol. 15, p. 50

an expression which is identical in form with the one which we have applied to the distribution of a gas between a solid and a liquid phase. He also calls attention to the fact that the general formula,

$$(x \text{ solid})^n/(x \text{ solution}) = \text{constant},$$

represents the condition of equilibrium, not only between charcoal and such substances as acids, etc., but between dyes and textile materials in contact with solutions of them. Zacharias* carried the matter further, and in a paper entitled "Über den Zustand und die Eigenschaften der Kolloide" not only discusses the absorption of dyes by textile materials, but points out the connection between such phenomena and the absorption of hydrogen by palladium. He considers that in such cases the condition of equilibrium may be arrived at by supposing that when the solid, or colloid as he considers it to be, is brought into contact with the gas or solution, the gas or solute diffuses into it, and forms a diffusion column, so that the concentration of it in the solid phase decreases as the distance from the surface increases.

There appears, however, to be no ground for the assumption that the modification of the simple law applies only to colloidal substances; rather it appears capable of application to any system in which one phase is rigid, and in which, in consequence, the law of distribution may be determined in some way by diffusion. Zacharias's analysis† relates to a state of steady flow across a surface, and not to a condition of equilibrium, and does not furnish mathematical proof that under the latter condition the logarithmic relationship would apply. As phases possessing rigidity we can describe crystalline solids, super-cooled liquids, and probably for this purpose colloidal, or jelly-like, masses, though the latter may, in themselves, consist of more than one phase. In my opinion such solid phases as we have considered fall under the second heading, and may be considered as being formed without discontinuity in their properties from the liquid phase. No analogous case of a crystalline solid appears to have been investigated.

It need scarcely be pointed out that such cases as that of the distribution of iodine between liquid and solid benzene‡ follow the simple law of distribution, the case in which $n=1$ in the general expression, for the reason that iodine does not diffuse into the solid benzene, but that the solid solution is formed directly from the liquid solution.

It is probable that the absorption of gases by the platinum which is "splashed off" from the electrodes of a vacuum-tube during the passage of the discharge takes place in a similar manner, each layer becoming saturated as

* 'Zeit. Phys. Chem.,' vol. 39, p. 468.

† *Loc. cit.*, p. 478.

‡ Van Bylert, 'Zeit. Phys. Chem.,' vol. 8, p. 343.

it is deposited. On heating, the gas is evolved, and as the metal appears to change at the same time from the amorphous to the metallic condition, the change is practically irreversible.

One might give many other examples of phenomena to which the terms "adsorption" and "occlusion" have been applied, and which may be explicable without the introduction of any principle other than that which we have been considering. To take one final example:—The value of n in the general expression, at any particular temperature, increases with the molecular complexity of the gas or substance in solution. Hence it is not surprising to find that when animal charcoal absorbs "colouring matters" from solutions of organic substances, the quantity of the latter which is removed from the solution appears to be proportional to the quantity of charcoal only, the latter being capable of removing practically the whole of the colouring matter if it is present in sufficient quantity. Further, if the charcoal has been too strongly heated it loses its power of absorbing colouring matters and, indeed, substances generally, either in the gaseous state or in solution, and this may be explained by the fact that the action of heat results either in the partial conversion of the carbon into a more stable crystalline phase, into which substances diffuse less readily, or in causing it to become more compact, in which case the surface is limited, and each "diffusion column" becomes longer.

[*Note added May*, 1906.—Within the last few weeks a paper entitled "Vapour Pressure in Equilibrium with Substances Holding Moisture"* has been published by Prof. Trouton, and as it may appear that he and I differ in the explanation of apparently identical phenomena, I have thought it advisable to append this brief explanation. Prof. Trouton's curves† are similar to those obtained by Hoitsema and referred to on p. 18. The lower portion of the PX isothermal curve for the system water-cotton appears to have the form represented by the equation $\sqrt[n]{P}/X = \text{const.}$, and so far as it is concerned Prof. Trouton suggests that "there is distinct indication of some further action or law coming into operation," that is to say, some law distinct from that which he has established for the upper portion of the curve.

The fact is, that while I have been considering the condition of equilibrium consequent on the formation of a diffusion column within the material of the "rigid phase," Prof. Trouton is concerned with the phenomenon of surface condensation, which implies the formation of a new phase. This new phase does not appear till a certain concentration of the component which suffers

* 'Roy. Soc. Proc.,' vol. 77, p. 292.

† *Loc. cit.*, p. 229.

distribution is reached in the rigid phase, and the new phase, as Prof. Trouton has shown, must be considered as bivariant till the film has attained a certain limiting thickness. It would be interesting to speculate as to the subsequent course of Prof. Trouton's curves, and I hope that his further researches will throw light on the subject.]

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*Effects of Self-induction in an Iron Cylinder.**

By Professor Ernest Wilson, King's College, London.

(Communicated by Sir William H. Preece, K.C.B., F.R.S. Received May 9,— Read June 7, 1906.)

If a solid cylindrical conductor be divided into imaginary concentric tubular conductors, the ordinary self and mutual induction theory shows that when the conductor is subjected to an alternating potential difference, the interior shells carry electric currents of smaller density than the exterior ones, and the currents suffer a phase displacement greater the nearer the centre of the cylinder. The theory shows that the permeability and conductivity of the material play an important part, the effects above mentioned being increased in magnitude with increasing permeability and conductivity. When, however, the material of the conductor has variable permeability the problem becomes more complicated, and it is the object of this paper to examine more closely what goes on in an iron cylinder when electric currents are reversed in it, and maintained steady after reversal. A second part of this research will deal with alternating currents of varying frequency and wave-form.

The cylinder employed is of mild steel and has a diameter and length each equal to 10 inches (25·4 cm.). It is provided with holes drilled in a plane containing its axis of figure in such a manner that exploring coils can be threaded to inclose certain portions of that plane. The exploring coils are three in number. They are each 2 inches wide in a direction parallel with the axis of figure and midway between the ends of the cylinder. Their depths in a radial direction are 1, 2, and 2 inches, and their average radii are 0·5, 2 and 4 inches respectively. These coils are referred to as Coils Nos. 1, 2, and 3, No. 1 being near the centre of the cylinder. The cylinder has been already described,† but for the purpose of

* In connection with this research, I wish to acknowledge a grant voted to me by the Council of the Royal Society out of the Government Grant Fund.

† 'Roy. Soc. Proc.,' vol. 69, p. 440.

the present research has had a hole ¼-inch diameter drilled through it coinciding with the axis of figure. At each end of the cylinder are two massive gunmetal projections, which in the present research serve to conduct the electric current into the cylinder. The conductors attached to these projections are connected to a reversing switch so constructed that at its mid position it short-circuits the circuit of the cylinder and its conductors, which were arranged in the form of a circle about 6 feet diameter. The electric current was supplied by storage cells through an adjustable resistance and the shunt of an ampère-meter. The potential difference of the cells and the adjustable resistance were such that on reversing the current in the cylinder its value in the main circuit remained constant. In fact, the reversal of the main current was practically instantaneous. The epoch of reversal was noted on a seconds clock and at two-second intervals after reversal the deflections of the dead-beat galvanometers in circuit with the exploring coils were noted. The deflections have been reduced to volts per turn per square centimetre of the coils from which they were obtained, and plotted in terms of the time. Figs. 1, 2, and 3 give the results obtained from Coils Nos. 1, 2, and 3 respectively, and each curve is numbered to correspond with the total ampères reversed when it was observed. The curves have been integrated in order to find the maximum average value of the induction density B for the respective coils. The average values are set out in Table I.

Current Density.

If the current density over the cross-section of the cylinder was constant, the force H would vary as the radius. If the values of B for Coil No. 3 in Table I be plotted in terms of the total currents reversed in the cylinder, it will be found that the resulting curve resembles the BH curve of a piece of mild steel. If the values of B for Coils Nos. 2 and 1 be plotted in terms of the total current multiplied respectively by 0·5 and 0·125 (to correspond with their radii), it will be seen that, although similar, the three curves do not lie on one another. To make them do so the coefficients with which to multiply the total currents are 0·75 and 0·28 respectively. This suggests that under steady conditions the current density is greater near the centre of the cylinder than near the surface. The average relative densities appear to be: (1) over the area of the cylinder within the average radius of Coil No. 1, 0·56; (2) over the annulus between the average radii of Coils Nos. 1 and 2, 0·36; (3) over the annulus between the average radii of Coils Nos. 2 and 3, 0·21. A total current of 950 ampères corresponds to an average force H of about 6 C.G.S. units for Coil No. 3, and the BH curve for mild steel is well

represented by the results of the experiments. The relation between the average value of H for each of the coils and the total current is given in Table I.

Table I.

Total current in cylinder.	Coil No. 1.		Coil No. 2.		Coil No. 3.	
	Av. H.	Max. av. B.	Av. H.	Max. av. B.	Av. H.	Max. av. B.
950	1·68	2640	4·5	8950	6·0	9640
670	1·18	1620	3·15	7300	4·2	8200
522	0·924	1040	2·48	6000	3·3	7060
424	0·75	660	2·01	4610	2·68	6210
356	0·627	540	1·69	3560	2·25	5420
240	0·426	200	1·14	1840	1·52	3420
210	0·372	—	0·998	1350	1·33	2520
160	0·283	100	0·758	773	1·01	1400
123	0·218	68	0·583	473	0·777	739
80	0·141	40	0·379	247	0·505	415
45	0·079	—	0·213	136	0·284	180

Comparison of E.M.F. Curves.

The E.M.F. curves are given in figs. 1, 2, 3, to which reference will be made. Coil No. 3 experiences its maximum rate of change at once, although after reversal of about 400 ampères there is slight evidence of a second maximum at about 20 seconds after reversal. After about 400 ampères it will be seen that as the total current increases the curves cross one another at shorter intervals, indicating that the effects penetrate more rapidly after the maximum average induction density has passed the value at which maximum permeability occurs.

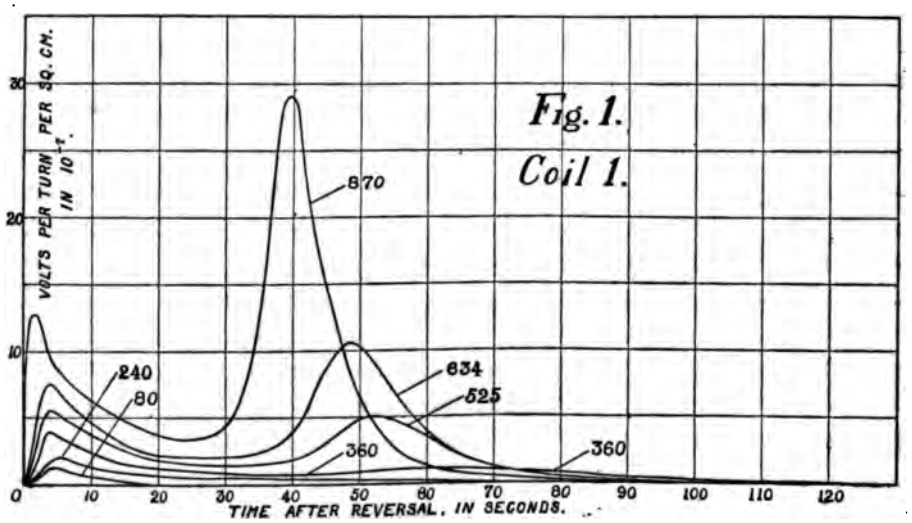


Fig. 1.

Coil 1.

Coil No. 2 shows the effect of a second maximum more markedly. When the total current in the cylinder is small there is no second maximum. At about 200 ampères the second maximum shows signs of being developed, and with larger currents its development is such as to make it the most important feature of the curves. As in the case of Coil No. 3, the E.M.F. curves cross one another at earlier intervals after about 420 ampères has been reached.

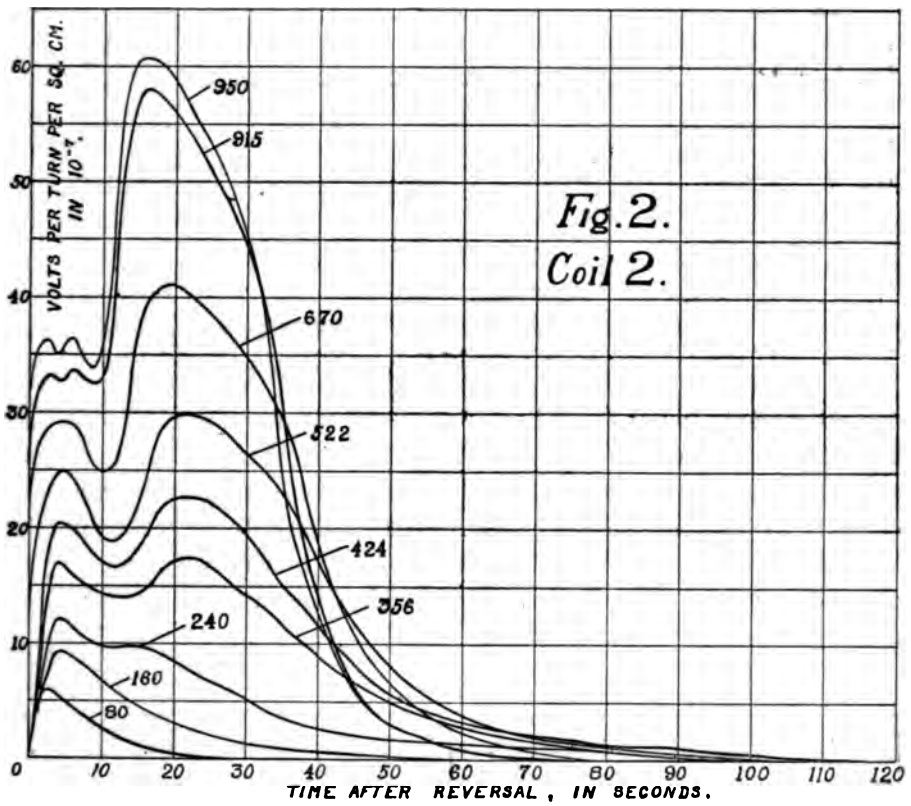
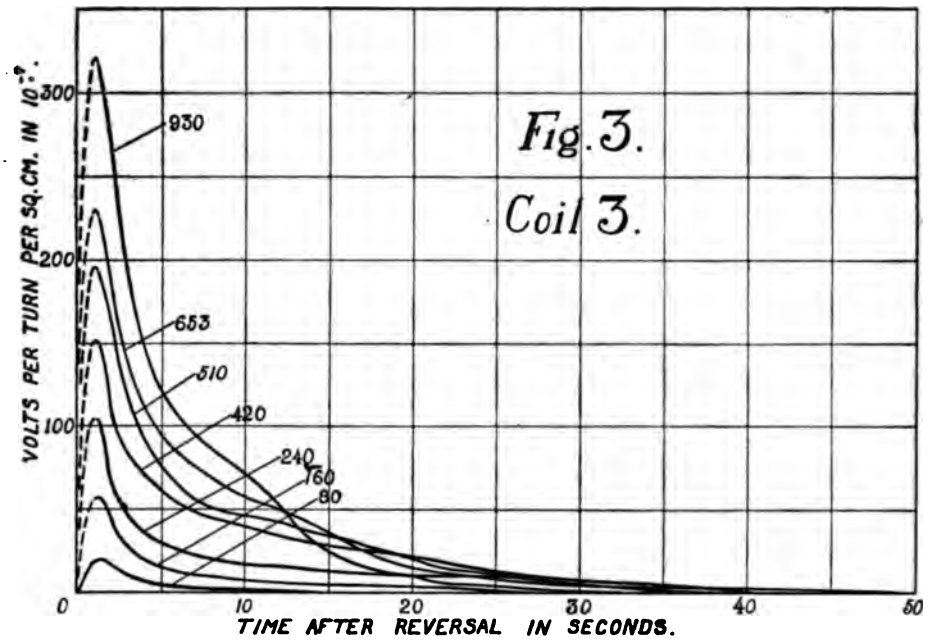


Fig. 2.
Coil 2.

Coil No. 1 shows similar effects, but its E.M.F.'s have a still later maximum for a given current. Moreover, the time between the first and second maxima is greater than in the case of Coil No. 2. These results are in keeping with what has already been observed in the case of the reversal of currents in a copper coil surrounding cylinders of 4 and 12 inches diameter,* and in the present cylinder when rotated in a magnetic field.† It is difficult to say exactly how long the effects take to die away owing to the ultimate want of sensibility of

* 'Phil. Trans.,' A, vol. 186 (1895), pp. 93—121; also 'Journ. Inst. Elec. Eng.,' Part 116, vol. 24, p. 194.

† 'Roy. Soc. Proc.,' vol. 69, p. 435, and vol. 70, p. 359.



the instruments, but a comparison of the times taken to practically die away is of interest. In Table II are given the times taken to reverse the magnetism at the centre of 4- and 12-inch diameter cylinders when the currents in their magnetising coils are instantaneously reversed, and then maintained steady. The times in these two cases roughly vary as the square of the diameters of the cylinders. The results obtained in the present experiments are also included in Table II.

Table II.

4-inch magnet.		12-inch magnet.		10-inch cylinder.			
Duration in seconds.	Max. H.	Duration in seconds.	Max. H.	Duration in seconds.			Total current in cylinder.
				Coil No. 1.	Coil No. 2.	Coil No. 3.	
40	1·7	360	1·2	—	20	—	45
45	3·0	420	2·4	20	28	15	80
33	4·96	180	6·0	30	48	30	160
10	16·0	80	11·0	58	80	50	210
5	37·0	50	24·0	75	100	—	240
				116	112	60	356
				120	120	50	424
				190	90	—	522
				90	75	40	670
				90	65	30	950

Upon integrating the E.M.F. curves it was found that the average magnetic flux, for total currents up to about 240 ampères, was reversed in sign for Coil No. 2 after Coil No. 1. For currents greater than 240 ampères the curves cross the axis of time in the order 3, 2, 1. In all cases, however, the total interior average currents, as obtained from the magnetic hysteresis loops, reversed in the order 3, 2, 1.

Application of Results to other Sections.

Comparing two cylinders whose diameters are as 1 : n, the value of H at similar radii will be the same when the total currents are as 1 : n. Considering unit length of the two cylinders, the total magnetic induction up to similar radii varies as n, and the electric resistance of similarly placed longitudinal paths varies as $1/n^2$. Therefore to induce n times the current in those paths the E.M.F.'s must vary as $1/n$. If the time varies as n^2 the E.M.F.'s will vary as $1/n$, thereby giving rise to the same value of the magnetic force H at similar radii.

A paper recently published* dealt with the self-induction of bull-headed railway rails, weighing 70 lbs. per yard. It was there shown how greatly the self-induction varies with the frequency for a given current, and with the current for a given frequency. The head of one of these rails is roughly equivalent to a cylinder of 2 inches diameter. A current of 100 ampères in such a cylinder corresponds to 500 ampères in our 10-inch cylinder if the forces at similar radii are to be the same. We infer roughly that an alternating current of 8 seconds periodic time and approximately rectilinear wave-form would permit of practically the whole section being made use of as regards conduction for a small fraction of the time of each half period. The frequencies employed in practice are of the order 25 periods per second, and are enormous by comparison. In railway work a ⊓-shaped rail would obviously be more suited from the standpoint of electric conduction of alternating currents.

A current of about 0·5 ampère in an iron wire of 0·1 inch diameter would give rise to a force of about 0·3 near the surface. Changes of magnetism in our 10-inch cylinder were observed 20 seconds after reversal of about 50 ampères. A frequency of 250 would allow of the full section of the wire being made use of during a small fraction of the time of each half period with 0·5 ampère, but not with a current of 5 ampères.

In conclusion, I wish to thank Mr. A. E. O'Dell for his patience and care in working out results, and Mr. H. W. Franks for his assistance in the experimental part of the paper.

* 'The Electrician,' February 23, 1906.

Some Physical Constants of Ammonia: a Study of the Effect of Change of Temperature and Pressure on an Easily Condensible Gas.

By Edgar Philip Perman, D.Sc., Assistant Professor of Chemistry, and John Hughes Davies, B.Sc., University College, Cardiff.

(Communicated by Principal E. H. Griffiths, F.R.S. Received April 24,—Read May 17, 1906.)

This work was originally undertaken in order to obtain an accurate value for the density of ammonia, the only determination that appeared reliable being that of Le Duc.* While the experiments were in progress, the result of a determination by Guye† was published; the number differed from that of Le Duc and made a fresh determination still more desirable. We have now determined the density at temperatures ranging from $-20°$ to $+100°$ C., also the density at half an atmosphere pressure at 0° C. From these data the coefficient of expansion and the compressibility can be calculated. In addition to this, measurements of the pressure coefficient, of vapour-pressure, and of the density of ammonia in the presence of air, have been made.

Vapour-density of Ammonia.

Two methods were employed:—

(1) The ammonia was pumped from the globe in which it was contained into concentrated sulphuric acid contained in U-tubes, and so weighed. The globe remained in position during each experiment.

(2) In a few experiments the ammonia was weighed directly.

Apparatus, Method (1).—The apparatus may be divided into three parts: (*a*) the ammonia supply, (*b*) the globe and bath, (*c*) the absorption apparatus:

(*a*) The ammonia was contained in an iron tube 20·5 cm. long and 3·5 cm. in diameter, closed by a valve B, obtained from the Scotch and Irish Oxygen Company. The outlet tube was connected by means of lead pipe (about 1 foot) and junctions of fusible alloy to the drying tubes C and D containing lime and recently fused sodium hydroxide respectively. The tube then divided into two branches, one leading to the escape tube E, about 900 mm. long, dipping under mercury, and the other to the globe G. Any

* 'Comptes Rendus,' 1897, vol. 125, p. 571.

† 'Comptes Rendus,' 1905, vol. 141, p. 51.

ammonia bubbling through the mercury was absorbed by dilute sulphuric acid contained in the wash-bottles F.

(*b*) The globe of about 1·8 litres capacity was placed in (1) a thermostat containing an Ostwald toluol regulator of special pattern,* (2) in an ice bath, (3) in a bath of alcohol and solid carbon dioxide, according to the temperature required. H was an ordinary stop-cock, and K a three-way tap leading to two sets of drying bulbs L, containing strong sulphuric acid. (Only one set is shown in the diagram.)

The temperatures above 0° were measured accurately to 0·02° by means of a thermometer made by Fuess, of Berlin, and standardised at the Reichsanstalt. For temperatures below 0° a mercury thermometer was used which had been previously standardised by comparison with an air thermometer. Owing to the difficulty of maintaining the constancy of these low temperatures, we cannot claim that they were accurate to less than 0°·1.

(*c*) The absorption apparatus consisted of three U-tubes, M, N, O, connected together by thick rubber tubing. M and N were stoppered. M was connected with a tube from the globe by the ground joint J, the U-tube being held in place by a rubber band. The tube O was connected with the gauge and a water air-pump not shown in the diagram. P and R were three-way stop-cocks.

Method of Work.

Filling the Globe.—Everything being in position, the globe and connecting tubes were exhausted to 0·1 mm. by means of a Töpler pump. The valve B was then opened until ammonia bubbled through the mercury in E, the taps H and K were opened, and left open until the ammonia again began to escape, when K was immediately closed.

The main part of the ammonia was then pumped out by the water air-pump through P, and the remainder by the mercury pump through R. It should be mentioned that the drying tube of the pump contained strong sulphuric acid, which immediately absorbed the ammonia thus admitted.

The globe was again filled as before. The temperature of the bath was carefully regulated, and the excess of ammonia allowed to escape into the air through P, the stop-cock R being turned on from time to time. Owing to the cooling caused by the expansion, some little time was required for the gas to acquire the exact temperature and pressure. From half an hour to an hour sufficed. In order to indicate when the pressure was equal to that of the

* 'Roy. Soc. Proc.,' 1903, vol. 72, p. 74.

atmosphere, a small mercury gauge was connected with J; it showed finally no change on turning R.

In some of the earlier experiments the water air-pump was used in the filling; in that case the globe was exhausted to 1/10 atmosphere and filled with ammonia, the process being carried out six times.

Absorption of the Ammonia.—The connecting tubes, including H, K, were freed from ammonia and moisture by repeated exhaustion and admission of air through L. The U-tubes containing sulphuric acid and glass wool plugs soaked with it (see fig. I) were then connected up, M and N having

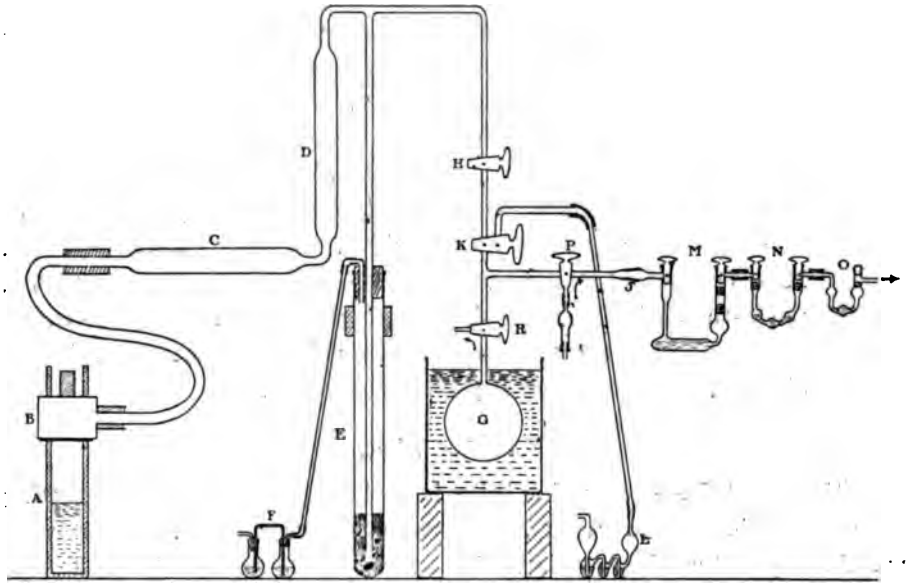


Fig 1.

been weighed; O was a guard tube to prevent the access of moisture from the pump. The connections were tested by exhausting the U-tubes and noting any change in the gauge on standing. Leaks having been shown to be absent, air was admitted through L, and the U-tubes were connected with the globe through P and R. The apparatus was then exhausted very slowly to about 1/10 atmosphere, very nearly all the ammonia being absorbed by the sulphuric acid in M; air was admitted through L, and the apparatus again exhausted. This was done five times in all. Next, air was admitted through L, and in order to make the pressure inside the tubes exactly that of the atmosphere, connection was made through a calcium chloride tube fixed to P; M and N were closed and then removed and carefully weighed. The barometer was read immediately after the ammonia

in the globe had ceased to blow off, the readings being made accurately to 0·1 mm.

Volume of the Globe.—The globe was weighed full of dry air at known temperature and pressure, and again full of water at known temperature. From these weighings the capacity of the globe was calculated. Correction was made for the displacement of air by the weights, and the weights used in this part of the work were compared with those used in weighing the ammonia (both sets having been compared with a standard gramme).

The coefficient of expansion of the globe was found by experiments with a weight thermometer made from a broken globe. Between 18°·5 and 100°·86 the coefficient was 0·0000251.

Method (2).—The ammonia was weighed directly in a globe of about 0·5 litre capacity. The weighings were made on a short beam Oertling balance, and were carried to 0·01 milligramme. The weights were standardised with the same accuracy.

In this case the globe was attached to the rest of the apparatus by means of a ground glass joint above the stop-cock; it was exhausted by a Fleuss pump to 0·01 mm., the pressure being read on a mercury gauge by means of a cathetometer. The empty globe was weighed, then filled with ammonia and detached. The excess of ammonia was allowed to escape, and the globe was again weighed, the usual precautions being taken throughout. A similar globe was used as a counterpoise.

The volume of the globe was found by weighing it, (*a*) completely exhausted; (*b*) full of dry air at known temperature and pressure; (*c*) full of water at known temperature. These measurements gave two closely concordant values for the capacity of the globe.

The contraction of the globe on exhaustion was measured as follows:—The globe was nearly filled with water, leaving about 5 c.c. of air in the upper part. This air was then pumped out and the stop-cock closed. The globe was next suspended in water and weighed to 0·01 gramme. It was opened to the air and weighed again, when it was found to have lost 0·15 gramme. The weight of air admitted was negligible.

Testing for Possible Errors.

Adsorption of Ammonia by Glass.—It has been usually supposed that a considerable quantity of ammonia is "adsorbed" by glass, the adsorption progressing for some time. If so adsorbed, it might be again evolved on exhausting the globe, or it might be held permanently by the glass. An experiment was made in which the globe was filled with ammonia above the atmospheric pressure, and allowed to stand 12 hours; the excess of

ammonia was then allowed to escape, and the usual number for the density was obtained. It is thus proved that if ammonia is adsorbed it is not given off on exhausting the globe.

As a further test a globe was filled with ammonia, exhausted to 0·1 mm., and allowed to stand. The pressure was then read at intervals for some days by means of a cathetometer, but it remained constant. Further, in determining the pressure coefficient, the same conclusion was arrived at, the pressure of the ammonia in an ammonia thermometer was not found to alter after the lapse of a month.

From these experiments we are forced to the conclusion that, with carefully dried ammonia and glass, adsorption (if it takes place at all) is inappreciable.

Condensation on the Surface of the Glass.—It has been thought that ammonia will condense in the same way as water vapour on the surface of glass, and so would cause an error in density determinations in glass globes. If this were the case, different densities should be obtained if globes of different sizes were employed. We have found, however, that globes of 0·50 litre and 1·77 litres capacity respectively gave the same result. The surfaces of these are as 1 : 2·31, whilst the volumes are as 1 : 3·51. The only conclusion to be drawn is that when the ammonia and the glass are carefully dried, there is no appreciable condensation of ammonia.

Loss of Ammonia by Incomplete Absorption.—The ammonia pumped out of the globe passed into two U-tubes containing concentrated sulphuric acid (including four plugs of glass wool soaked with acid), but as in all the exhaustions, except the first, the ammonia was mixed with a large proportion of air, it was thought possible that traces of ammonia might nevertheless escape absorption. This was tested by allowing the mixture of air and ammonia at the second and the fourth exhaustions to pass through two U-tubes into an exhausted globe. The contents of the globe were then tested for ammonia by Nessler's solution, but *not a trace was found.*

Moisture from the Air.—The air made to expel the ammonia was first passed through two "potash bulbs" containing strong sulphuric acid, and the bulbs were recharged every day. On passing 5 litres of air the weight of the U-tubes remained unaltered, thus showing that none of the moisture escaped absorption.

Evaporation of Sulphuric Acid.—In order to test whether any sulphuric acid was lost by evaporation, about 8 litres of dry air were passed through the first U-tube, the sulphuric acid contained in it being heated to about the same temperature as it acquired during the absorption process. *The weight remained constant to* 0·1 *milligramme.*

Displacement of Air owing to Change in Volume of Sulphuric Acid caused by Absorption of Ammonia.

After the completion of an experiment, the density of the contents of the U-tube was determined, and also that of the original sulphuric acid:—

	grammes.
25 c.c. specific gravity bottle	14·29
sp. gr. bottle + H_2SO_4 + NH_3 after expt.	60·27
H_2SO_4 + NH_3 filling bottle	45·98
sp. gr. bottle + fresh H_2SO_4	59·10
Fresh H_2SO_4 filling bottle	44·81

If no change in volume of acid had taken place, weight of mixture filling bottle would be 44·81 + 1·38 = 46·19 grammes (1·38 grammes = weight of NH_3 absorbed).

Change in volume produced by absorption of NH_3

$$= \frac{46{\cdot}19 - 45{\cdot}98}{46{\cdot}19} \times 25 = 0{\cdot}1 \text{ c.c. approximately.}$$

The correction for air displaced is therefore 0·00013 gramme.

Preparation of Ammonia.

Ammonia from various sources was employed:

(1) Commercial anhydrous ammonia from an iron cylinder.

(2) Commercial ammonia was passed through a hard-glass tube containing red-hot lime into pure hydrochloric acid; the ammonium chloride formed was heated with solution of sodium hydroxide, and the ammonia evolved was thoroughly dried by passing over quick lime and sodium hydroxide. This method was used by Guye.* In our early experiments the ammonia was condensed in a glass tube placed in a freezing mixture of ether and solid carbon dioxide; later an iron tube was used.

In order to prove the efficacy of this method of preparation in destroying pyridine, a slow stream of hydrogen was bubbled through this liquid contained in a small wash-bottle, and then passed over red-hot lime. No pyridine could be detected in the gases leaving the hard-glass tube.

A sample of ammonium chloride made by the above-mentioned method was very kindly subjected to spectroscopic examination by Dr. J. J. Dobbie, who reported that he found no indication of the presence of pyridine.

(3) Dobbie has shown† that ammonium oxalate can be freed from pyridine by repeated recrystallisation. Some ammonium oxalate was made

* *Loc. cit.*

† 'Chem. Soc. Journ.,' 1900, Trans., vol. 77, p. 318.

from commercial oxalic acid and ammonia and recrystallised 10 times (another sample six times, which proved sufficient); the ammonia was set free by heating with potash, and condensed in a glass tube.

(4) Sodium nitrite was reduced with aluminium and sodium hydroxide solution; the ammonia was absorbed by hydrochloric acid, and again liberated by sodium hydroxide.

The main part of the ammonia used was made by method (2), and was condensed in the iron tube (see diagram) placed in ether and solid carbon dioxide. The tube was fitted up like a wash-bottle, the ammonia passing in through the long tube. To the short tube was connected a drying-tube to prevent the entrance of moisture from the air. When a sufficient quantity of ammonia had condensed, the tube was removed from the freezing mixture, placed in a vice, and the valve immediately screwed on, a leather washer being placed between the tube and the valve. The valve was then fully opened, and left for about 5 minutes in order to expel the air from the top of the tube by the rapid stream of ammonia.

After some preliminary experiments the following results were obtained:—

Method (1).

Commercial Ammonia.—Temperature 0°. Capacity of globe 1·7738 litre.

Mass of ammonia.	Barometer.	Mass of 1 litre at 760 mm.
grammes.	mm.	gramme.
1·3832	767·9	0·7718
1·3838	768·05	0·7719
1·3825	767·2	0·7721
1·3843	768·2	0·7721
Mean		0·7720
Corrected to latitude 45° and for expansion of sulphuric acid on neutralisation		0·7717

Temperature 0°. Capacity of globe 1·7738 litre.

Source of NH_3.	Mass of ammonia.	Barometer.	Mass of 1 litre.
	grammes.		
(2)	1·3814	767·8	0·7709
	1·3830	768·5	0·7711
(3)	1·3325	740·3	0·7712
	1·3361	742·2	0·7713
(4)	1·3696	760·8	0·7713
	1·3637	760·0	0·7711
	1·3626*	756·3	0·7713
Mean finally corrected			0·77085

* Left for 12 hours to test adsorption.

Method (2).

Capacity of globe 504·76 c.c. Temperature 0°.

Mass of ammonia.	Barometer.	Mass of 1 litre.
gramme.	mm.	
0·39206	765·7	0·77094
0·39349	768·5	0·77094
0·39306	767·7	0·77090
0·39433	770·2	0·77088
Mean		0·77091
Corrected for contraction of globe when exhausted		0·77127
Reduced to latitude 45°		0·77086

The results now available for the vapour-density of ammonia at 0° are:—

Le Duc	0·7719	Reduced to lat. 45° and sea-level.
Guye	0·7708	
Perman and Davies (1)	0·77085	
„ „ (2)	0·77086	

We may venture to say that Le Duc's number is erroneous, owing to the use of unpurified ammonia. Our final result is 0·77085 (giving the greater weight to series (1)), which differs only by about one part in 15,000 from that obtained by Guye, and may be taken, we believe, as the most accurate value yet obtained for this constant.

Density of Ammonia at 50°.—Capacity of globe 1·7760 litres.

Mass of ammonia.	Barometer.	Mass of 1 litre.
grammes.	mm.	gramme.
1·1190	740·6	0·6466
1·1297	747·9	0·6464
1·1476	759·6	0·6466
1·1599	767·7	0·6466
Mean		0·64655
Mean finally corrected		0·64627

Density of Ammonia at 100°.—Capacity of globe (new) 1·7718 litres.

Mass of ammonia.	Barometer.	Mass of 1 litre.
gramme.	mm.	gramme.
0·9881	760·8	0·5571
0·9913	763·8	0·5568
0·9936	765·1	0·5570
0·9931	765·2	0·5568
Mean		0·556925
Mean finally corrected		0·55668

Density of Ammonia at $-20°$.—The temperature $-20°$ was obtained by shaking solid carbon dioxide into a bath of alcohol surrounded by thick felt and thoroughly stirred. The temperature was read on a mercury thermometer and was maintained constant within $0°{\cdot}1$ by adding solid carbon dioxide in small quantities as required. The thermometer was standardised by means of an air thermometer.

Capacity of globe 903·20 c.c.

Mass of ammonia.	Barometer.	Mass of 1 litre.
gramme.	mm.	gramme.
0·7612	765·9	0·8363
0·7599	763·9	0·8370
0·7586	763·2	0·8364
0·7522	756·7	0·8364
Mean		0·8365
Mean finally corrected		0·8363

Coefficient of Expansion of Ammonia.—From the results just given the specific volumes are:—

Temperature.	Volume of 1 gramme.
$-20°$	1·19575 litres
0	1·2973 „
50	1·5473 „
100	1·7964 „

From these numbers the coefficients of expansion for different ranges of temperature have been calculated:—

Temperature.	Coefficient of expansion.
Between $0°$ and $-20°$	0·003914
0 +50	0·003854
0 100	0·003847

The coefficient is seen to be much greater than that of the less easily condensible gases, and decreases with rise of temperature. Attempts were made to calculate values of a and b in van der Waals' equation from these data; it was found, however, to be impossible, the equation not representing the facts with sufficient accuracy. Taking the simple equation $pv = RT$ R is found to vary about 2 per cent. between $-20°$ and $100°$.

Temperature.	R.
−20°	0·004726
0	0·004752
50	0·004790
100	0·004816

p is here expressed in atmospheres and v in litres.

Compressibility of Ammonia.—By comparing the density at half an atmosphere with that at one atmosphere, the compressibility of ammonia may be determined. The globe was filled with ammonia in the usual way, then connected with a pressure-gauge and about half the ammonia pumped out. Next the ammonia was allowed to blow off until equilibrium had been attained, when the pressure was immediately read. The readings were made on a mirror scale, the barometer standing in the same trough being read at the same time (see fig. II). Owing to the difficulty of reading the pressure and maintaining its constancy, no great accuracy was attained; the probable error is about 0·2 mm.

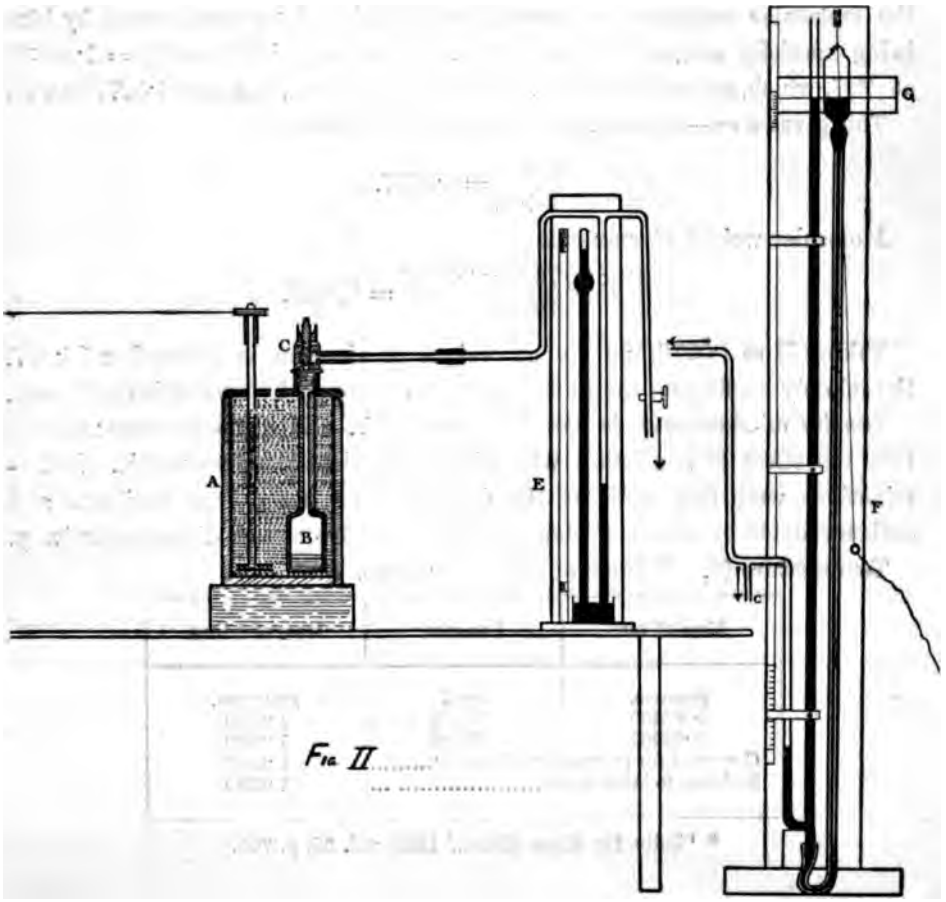


FIG. II.

Density of Ammonia at Half an Atmosphere.—Capacity of globe 1·7738 litres. Temperature 0°.

Mass of ammonia.	Pressure.	Mass of 1 litre at 380 mm.
gramme.	mm.	gramme.
0·6888	385·1	0·3832
0·6859	383·1	0·3835
0·6696	374·4	0·3832
0·6811	380·6	0·3834
Mean		0·3833
Corrected for contraction of globe, expansion of acid, and latitude		0·3832

From these results

$$\frac{pv \text{ at } \frac{1}{2} \text{ atmos.}}{pv \text{ at 1 atmos.}} = \frac{380 \times 2{\cdot}6096}{760 \times 1{\cdot}2973} = 1{\cdot}0058 = \mathrm{B}.$$

As before stated, we cannot claim any great accuracy for this result, and we prefer to make use of Lord Rayleigh's number in proceeding to calculate the molecular weight of ammonia, the method and apparatus used by him being specially adapted to the purpose.* Lord Rayleigh found B = 1·00632 at 9°·7, which, corrected in the way indicated by him, becomes 1·00706 at 0°.

This gives $\alpha = -0{\cdot}01413$, and the correction factor

$$\frac{1+\alpha}{1+\alpha_0} = 0{\cdot}9867.$$

Molecular weight of ammonia

$$\frac{32 \times 0{\cdot}77086 \times 0{\cdot}9867}{1{\cdot}4292} = 17{\cdot}030.$$

Taking H = 1·0076, the atomic weight of nitrogen is deduced as 14·007, thus closely confirming the number obtained recently by several investigators.

Density of Ammonia in the Presence of Air.—Experiments were made to test the effect of admixture with air on the density of ammonia. Determinations were first made of the density of air freed from moisture and carbon dioxide by means of phosphorus pentoxide and soda-lime respectively.

Temperature 0°. Volume of globe 504·76 c.c.

Mass of air.	Pressure.	Mass of 1 litre.
gramme.	mm.	grammes.
0·65420	762·2	1·2923
0·65280	760·6	1·2923
Corrected for contraction of globe		1·2927
Reduced to latitude 45°		1·2920

* 'Zeits. für Phys. Chem.,' 1905, vol. 52, p. 705.

The globe was exhausted and weighed, about half filled with ammonia, and weighed again. It was then surrounded with ice, and air carefully admitted until the mixture had attained the atmospheric pressure. Another weighing was then made. The following are the data:—

Temperature 0°. Volume of globe 504·76 c.c.

Mass of NH_3.	Mass of air.	Total pressure.	Partial pressure of air.	Partial pressure of NH_3.	Mass of 1 litre ammonia at 380 mm.
0·18017	0·34481	755·7	401·8	353·9	0·38326
0·20274	0·31924	770·3	372·0	398·3	0·38320
		Mean corrected for latitude			0·38308

The density calculated from Rayleigh's value for the compressibility (B = 1·00706) is 0·38272. The partial pressure of the ammonia in the above table is obtained by subtracting the partial pressure of the air (calculated from its weight) from the total pressure. It will be seen that the density is nearly one part in 1000 higher than that calculated from the compressibility, and this represents the deviation from Dalton's law of a mixture of approximately equal volumes of ammonia and air.

The normal value of the density of ammonia, calculated from its molecular weight and the density of oxygen, is 0·7605; consequently the density of ammonia is still about 1 per cent. above the normal value, even when diluted to the extent mentioned.

Pressure-coefficient of Ammonia.—A simple form of constant volume air-thermometer, with a globe of about ½ litre capacity, was filled with pure ammonia at about 15° C., and atmospheric pressure. In order to test if there were any inaccuracy caused by adsorption, successive readings were taken at an interval of 48 hours at 98°·1, of 24 hours at 80°, and of a month at 20°, but the readings in each case agreed within the limits of experimental error. Allowance was made for the expansion of the globe with rise of temperature. The correction for the tube connecting the globe and the gauge was inappreciable. The following are the results (see p. 40).

It will be seen at once that the numbers show a considerable deviation from van der Waals' equation, which may be written in the form $p = KT - C$, where K and C are constants: K is proportional to the pressure-coefficient and varies, therefore, by nearly 6 per cent. over the range of temperature employed.

The values of the pressure-coefficient are, as would be expected, very close to those obtained for sulphur dioxide, and higher than those for carbon dioxide or nitrous oxide.

Date.	Pressure corrected for temperature of mercury.	Pressure corrected for expansion of globe.	Temperature.	Pressure coefficient.
February 17	988·9	991·3	98°·1	0·003802
„ 19	988·7			
„ 19	939·8	941·7	80	0·003804
„ 20	939·9			
„ 20	886·55	887·9	60	0·003830
„ 20	832·4	833·2	40	0·003850
„ 20	778·0	778·4	20	0·003906
„ 20	664·5	664·2	−20	0·004003
„ 21	722·0	—	0	—
March 24	777·9	778·3	20	0·0039055

Summary.

(1) The vapour density of ammonia at 0° has been found to be 0·77085 (mass of 1 litre in grammes at latitude 45°), previous results being 0·7708 by Guye and 0·7719 by Le Duc.

(2) When the ammonia and the glass vessel were thoroughly dried no appreciable adsorption of ammonia by glass, or condensation of ammonia on the surface of glass, was found to take place.

(3) From density determinations at different temperatures, the coefficient of expansion of ammonia has been deduced as 0·003914 between 0° and − 20°, and 0·003847 between 0° and 100°.

(4) From Rayleigh's determination of the compressibility of ammonia and our own value for the density, the molecular weight of ammonia has been calculated as 17·030, and the atomic weight of nitrogen as 14·007.

(5) Incidentally the density of air free from water vapour *and carbon dioxide* has been determined as 1·2920 (lat. 45°).

(6) The deviation from Dalton's law for a mixture of approximately equal volumes of air and ammonia has been found to be about 1 part in 1000.

(7) The pressure-coefficient of ammonia has been determined, the pressure being atmospheric at 15°. Between 0° and − 20° the coefficient was 0·004003, and between 0° and 98° it was 0·003802.

The expenses incurred in the above research have been defrayed by a grant from the Royal Society.

Appendix.

Vapour Pressure of Liquid Ammonia and the Determination of its Boiling Point.

By John Hughes Davies.

It was suggested to me by Dr. Perman, to whom I am much indebted for kindly advice and assistance, that I should repeat the determination of the vapour pressure of liquid ammonia at some of the lower temperatures, using *pure* ammonia, in order to obtain an accurate value for its boiling point.

Apparatus.—(Fig. 2.) This consisted of:—

1. The bath A, which was a cylindrical zinc pot about 10 inches high and 6 inches diameter, covered completely on the outside with a coating of very thick felt. It contained alcohol and solid carbon dioxide, and was provided with a stirrer worked by a hot-air motor.

2. The iron tube B, which contained the liquid ammonia. This differed from the tube previously described (A, fig. 1) only in having a narrow stem.

3. The pressure gauge. Two forms of gauge were used, one for the lower temperatures, *i.e.*, temperatures at which the pressure was less than atmospheric, and the other for the higher temperatures and pressures. The former is indicated in the diagram by E and the latter by F. The pressure was read on a millimetre scale. G is a movable glass mirror of rectangular shape with a horizontal line drawn across it; by sliding it along the edge of the scale, and behind the glass tubes of the gauge, the pressure could easily be read to 1/10 mm.

4. The thermometer. A pentane thermometer was employed; it was graduated in single degrees, so that the temperature could be read accurately to 0°·1. It was standardised by means of an air thermometer.

Method of Procedure.—The apparatus being in position with the suitable pressure gauge attached and the steel valve shut off, the leading tubes were exhausted to 1/10 mm. by means of a Fleuss pump, exhaustion taking place through the stop-cock in the case of the gauge E and through the side tube C in the case of gauge F. The stop-cock was then turned off, or the side tube drawn out and fused, as the case might be. The bath was brought down to the required temperature by the addition of solid carbon dioxide, the valve C turned on, the pressure indicated by the gauge read, and the temperature of the mercury in the gauge taken.

Results.—Determinations were carried out over the range of temperature −50° to −5°.

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible] the values of the vapour pressures at equal intervals of [illegible] have been obtained by graphical interpolation.

[illegible]	[illegible]	[illegible]	[illegible]
	mm.		mm.
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible] were obtained from the curve, while the [illegible] were directly observed. From this curve the boiling point of liquid [illegible] is found to be —[illegible]° C.

The vapour pressures are found to be in very good agreement with those obtained by Regnault* and Ferche,† while they differ considerably from those obtained by Ramsay and Young.‡ Also the value obtained for the boiling point, viz., —[illegible]°, is in close agreement with the value —33°·46 obtained by H. B. Dixon.§

* 'Viola' Landolt and Bornstein Tabellen,' 1905 edition, pp. 77, 78.
† 'Viola Ibid.
‡ 'Phil. Trans.,' 1885, p. 155.
§ 'Wied. Ann.,' vol. 24, p. 10, 1885.
‖ 'Amer. Chem. Soc. Journ.,' vol. 27, p. 851, 1905.

Barometric Variations of Long Duration over Large Areas.

By WILLIAM J. S. LOCKYER, M.A., Ph.D., F.R.A.S., Chief Assistant, Solar Physics Observatory, South Kensington.

(Communicated by Sir Norman Lockyer, K.C.B., LL.D., Sc.D., F.R.S. Received May 8,—Read June 21, 1906.)

[PLATES 1—5.]

In a paper* communicated to the Society in the year 1902, Sir Norman Lockyer and I pointed out the existence of a barometric see-saw of short duration† (about 3·8 years) occurring between two large regions, nearly antipodal to each other, the centres of which were approximately India and Cordoba (South America). A continuation of the research indicated that this barometric see-saw was of greater extent than was at first supposed, and in a further communication‡ in the same year observations extending over new regions were discussed and the results published. Still further inquiry indicated that this see-saw was almost world-wide in its extent, and the result of a later investigation, which included the examination of pressure observations at 95 stations scattered over the earth's surface, was communicated§ to the Society in the year 1904.

During the progress of this work it was noticed that many of the curves representing barometric changes over a great number of years in various widely distributed areas exhibited variations of much longer duration which were neither coincident in their epochs of maxima or minima or even in the lengths of their oscillations.

It seemed to me therefore quite possible that if a distinct pressure change of short duration could occur simultaneously, but of opposite phase, in anti-

* 'Roy. Soc. Proc.,' vol. 70, p. 500.

† The use of the word period previously employed in these investigations did not *necessarily* imply that the curves discussed were *perfectly* "*regular*" but that the meteorological variations which they represented showed oscillations which, when more will be known about them, may possibly be found to be dependent on a periodic cause or causes.

The sun-spot variation, for instance, is generally described as being periodic, with a period of 11·1 years. As a matter of fact this is only a *mean* value of the intervals, minimum to minimum, the departures from this mean amounting sometimes to two years. Such differences from the mean may be due to other underlying periods, one of which of about 35 years in length was suggested in my paper entitled "The Solar Activity 1833—1900," communicated to the Royal Society in 1901, 'Roy. Soc. Proc.,' vol. 68, p. 294.

‡ 'Roy. Soc. Proc.,' vol. 71, p. 134.

§ 'Roy. Soc. Proc.,' vol. 73, p. 457.

podal parts of the earth it was not unreasonable to expect variations of long duration to behave in a like manner. The question was, however, well worth inquiring into, and the object of this communication is to present to the Society the first results of the investigation. In the present instance the survey does not extend over the whole world, but is restricted to the areas which include India, the East Indies, Australia and South America. It may be stated further that, for such an investigation as this, as long a series of homogeneous observations as possible for each station is desirable. The available data are, however, not so numerous as would have been wished, but in spite of this I think that the results deduced are sufficiently consistent to serve as a first approximation to the barometric changes in operation in these areas. The paucity of barometric data is most conspicuous in the South American region, so that for this part of the world the change of long duration has to be deduced from several portions of series of observations made at various stations. This I am aware is not a very satisfactory procedure, but failing this no other means is available.

In a previous communication* curves have been published representing barometric changes of short duration for Bombay, Cordoba and Adelaide, commencing in the years 1873, 1873 and 1876 respectively.

Since the curves for Bombay and Adelaide can be carried much further back than the above dates, namely to 1847 and 1857 respectively, I have considered it necessary and advantageous to bring together in the first instance a series of curves representing the short period variation for the regions dealt with in this paper. Further, two or more independent curves are given for each area investigated, in order to demonstrate the real nature of such variations.

Plate 1 gives seven curves exemplifying the variations of the mean annual pressure changes from year to year. Madras and Bombay represent India, Batavia the East Indies, Melbourne and Adelaide are typical of Australia, and Cordoba and Santiago show the changes in the South American region.

Since the barometric variation of short duration of the last two mentioned places is of opposite phase to that occurring in the Indian area, these two curves representing their changes have been inverted in the plate.

The curves are all drawn on the *same* scale, so that a quantitative as well as a qualitative idea may be obtained of the amplitudes of the variations in these different and widely distributed regions.

It is only necessary to take a rapid glance at this series of curves to form an idea of the very close relationship that exists between the barometric

* 'Roy. Soc. Proc.,' vol. 73, Plate 13.

changes in these parts of the world. As the curves indicate, the changes are of the greatest magnitude in the Australian area, while in the East Indies, India and South America, they are more or less of the same order of intensity. This magnitude, although for a great part dependent on the geographical positions of the areas as regards latitude, is not apparently entirely so, since there is a great difference between the values for the Cordoba and South Australian stations, the latitudes of which are approximately the same. In a subsequent paragraph reference will be made to the effect of latitude on the percentage values of the amplitudes of the variation of short duration in terms of the mean annual swing.

To determine approximate relative magnitudes of the largest amplitudes of these changes of short duration for these regions, the five most prominent rises in the curves from a minimum to a succeeding maximum have been selected and the differences of the readings determined. In the case of Madras and Bombay the means are respectively 0·033 and 0·036 inch, which give for the Indian area a mean maximum amplitude of 0·035 inch.

The individual years taken and the corresponding barometric readings were as follows :—

Station.	Year.	Minimum.	Year.	Succeeding maximum.	Difference.
		inches.		inches.	
Bombay	1862	29·778	1864	29·827	
	1875	29·812	1877	29·848	
	1878	29·801	1881	29·825	
	1886	29·812	1888	29·836	
	1898	29·795	1899	29·830	
Mean	...	29·800	...	29·833	0·033
Madras	1862	29·806	1864	29·851	
	1875	29·814	1877	29·866	
	1882	29·806	1884	29·840	
	1887	29·810	1888	29·836	
	1898	29·805	1899	29·828	
Mean	...	29·808	...	29·844	0·036

For three stations in Australia the values for the amplitudes, derived in a similar manner, are 0·076 inch for Melbourne, 0·077 inch for Adelaide and 0·071 inch for Sydney, the mean value for Australia being 0·074 inch. The values from which these means have been derived are as follows (see p. 46).

Comparing the means for the Indian and Australian regions, it is seen that the ratio of amplitudes is as 35 to 74, that is as 1 to 2 nearly.

Station.	Year.	Minimum.	Year.	Succeeding maximum.	Difference.
		inches.		inches.	
Melbourne	1868	29·896	1866	29·954	
	1875	29·886	1877	29·993	
	1878	29·905	1881	29·966	
	1882	29·902	1885	29·996	
	1890	29·924	1891	29·985	
Mean	...	29·903	...	29·979	0·076
Adelaide	1868	30·006	1865	30·078	
	1875	30·028	1877	30·144	
	1879	30·052	1881	30·107	
	1882	30·047	1885	30·121	
	1890	30·036	1891	30·111	
Mean	...	30·034	...	30·111	0·077
Sydney	1867	29·872	1868	29·933	
	1875	29·803	1877	29·896	
	1879	29·816	1881	29·874	
	1882	29·829	1885	29·920	
	1893	29. 829	1894	29·885	
Mean	...	29·830	...	29·901	0·071
General mean...	...	...	...	...	0·074

This fact seems to me of very great importance, because, if these barometric changes of short duration are on so much larger a scale in Australia than they are in India, a study of the Australian conditions may materially assist Indian Meteorologists.

The amplitude for the South American region is of about the same order as that of India, the mean for five stations derived in the above-mentioned manner being 0·38 inch. The individual stations and corresponding values are as follows (see opposite page).

The first step taken to render more apparent the changes of long duration involved in all these curves was to eliminate as far as possible the prominent short variations of about four years' duration. This was to a great extent accomplished by grouping the years in sets of four and employing the mean values of each of these groups. Thus the means for the years 1873 to 1876 1874 to 1877, 1875 to 1878, and so on, were determined, and curves were drawn through each of these points after they had been plotted on squared paper. Each mean point was actually plotted on the time scale at the end of the second year of the group of which it was the mean. Thus the mean for 1873 to 1876 was plotted at the end of 1874.

The curves first dealt with in this manner were those showing the pressure changes for India. Although one curve would have been sufficient to

illustrate the variation over this area, a second curve is added to serve as a check on the accuracy of the first. For this region the barometric observations made at Bombay and Madras were utilised since they go back so far as 1847 and 1842 respectively.

Station.	Year.	Minimum.	Year.	Succeeding maximum.	Difference.
		inches.		inches.	
Cordoba	1873	28·494	1875	28·534	
	1884	28·498	1886	28·532	
	1888	28·499	1890	28·531	
	1891	28·508	1893	28·552	
	1902	28·487	1903	28·522	
Mean	...	28·497	...	28·534	0·037
Curityba	1887	27·008	1888	27·043	
	1891	27·028	1894	27·055	
	1899	27·031	1900	27·055	
	1902	27·031	1903	27·057	
Mean	...	27·025	...	27·053	0·028
Goya	1877	29·782	1878	29·832	
	1888	29·805	1890	29·840	
	1891	29·828	1893	29·858	
Mean	...	29·805	...	29·843	0·038
San Juan (Buenos Ayres)	1868	29·892	1871	29·943	
	1873	29·930	1874	29·979	
	1877	29·906	1878	29·946	
	1887	29·880	1889	29·923	
	1891	29·908	1893	29·954	
Mean	...	29·903	...	29·949	0·046
Santiago	1871	28·235	1872	28·269	
	1877	28·185	1879	28·235	
	1888	28·217	1890	28·238	
	1900	28·176	1901	28·232	
	1902	28·182	1903	28·230	
Mean	...	28·199	...	28·241	0·042
General mean...	...	...	...	...	0·038

These two curves are reproduced on Plate 2 and it will be seen that they are very nearly identical in every respect. They exhibit, further, variations of a periodic nature, but this periodicity becomes much less apparent after the year 1880. The next curve examined was that of Batavia (East Indies). Unfortunately the observations do not go back further than 1866, but where the curve overlaps those of India the close similarity of the changes is very apparent.

Going still further away from India, the Australian continent was then examined. Here the curves representing the variation of long duration begin to present a new aspect.

Fortunately three excellent series of barometric observations are available for this region, namely, those for Adelaide, Melbourne, and Sydney, commencing respectively in the years 1857, 1859, and 1858. The changes at Perth are also included here, as there is a set of observations commencing in 1876 which represent the variations taking place well to the west of this continent.

All these four curves are reproduced on the *same* scale in Plate 2. It will be seen in the first instance that the Adelaide curve resembles in a general way that of Bombay and that the maximum about the years 1877 and 1878 is almost equally pronounced in Adelaide. Attention is specially drawn to this particular maximum, as it will be observed when examining the curves for Melbourne, Sydney, and Perth, that during these years it becomes of quite secondary importance.

If for the moment the curves at this epoch be left out of consideration, it will be seen that the remaining portions of all the curves are not only very like each other, but bear a general resemblance to those of the Indian region.

Before dealing with the possible origins of these barometric variations of long duration in the eastern hemisphere, attention will first be directed to a part of the western hemisphere, namely, that of South America, to see whether similar changes are in operation there, and if so, to study their nature.

It will be remembered that the barometric change of short duration in this region behaved in an *inverse* manner to that of the Indian and Australian areas (see Plate 1).

Unfortunately for this part of the world data are not numerous, but still, I think they are sufficient on the present occasion not only to demonstrate that a long barometric variation does take place, but that the epochs of maxima and minima are not those of either India or Australia as deduced in this paper.

Employing the same method as above described, four-year means were determined and curves drawn for the five stations, Cordoba, Goya, and San Juan (Argentine Republic), Santiago (Chili), and Curityba (Brazil). All these curves are reproduced in Plate 3, and are drawn on the *same scale* as those of the Indian and Australian curves in Plate 2.

Although the South American curves extend over different periods of time, there is sufficient overlapping in all cases to connect up one series with another.

The Cordoba curve undoubtedly indicates that a long barometric change is taking place, but the shortness of the period over which the observations extend, namely, from 1873 to 1904, renders it unserviceable for the determination of its possible periodicity. A neighbouring station, Goya, corroborates in a general manner, so far as the observations extend, the Cordoba variation, with perhaps the exception of the first three points on the curve.

To carry back these pressure changes to an earlier date, the observations at San Juan (Buenos Ayres) were employed; the available data for this station extend from 1867 to 1889. Here we find the fall of pressure at Cordoba from 1875 to 1882 well corroborated, followed by a subsidiary maximum similar to that at Goya in 1885. So far as these observations extend, there seem to be two prominent maxima at about the epochs 1874 and 1893, each of which is followed by minima at about the years 1882 and 1901.

The curve for Santiago, a station to the west of the Andes, indicates also very clearly these two principal maxima and the second of the two minima at the same epochs, but the minimum about the year 1882 occurs somewhat earlier.

At a station in Brazil, Curityba, in which only a short series of observations is available, this long variation is also in existence; the second principal maximum, however, falls a little later than at the previously mentioned stations.

In order to indicate generally the approximate dates of the occurrence of the points of maxima and minima in these four-year mean curves, the following table has been drawn up. In this the large type figures represent the years of the most prominent maxima and minima, while those in smaller type indicate those of a subsidiary or uncertain nature:—

Years of maxima.					Years of minima.				
India.	Batavia.	Adelaide.	Perth, Melbourne, Sydney.	South America.	India.	Batavia.	Adelaide.	Perth, Melbourne, Sydney.	South America.
1845	—	—	—	—	1849	—	—	—	—
1857	—	—	—	—	1862	—	1862	1863	—
1867	—	1867	1868	—	1871	1872	1871	1875	—
1877	1877	1878	1878	1874 —	1881	1881	1881	1881	—
1886?	1884?	1887	1887	—	—	—	—	—	1882
1901?	1901?	(1901?)	—	1893 —	1894 —	1894 —	1894 —	1894 —	— 1901

Generally speaking, the above figures indicate that while the Indian and Batavian (and Adelaide) curves show a variation, the duration of which is somewhere about 11 years, the curves for the other Australian stations and those of South America present a change in which the maxima and minima are about 19 years apart. Reference to these changes will be made more fully in subsequent paragraphs.

It is important further to note, as was done in the case of the variation of short duration, the very great difference between the *amplitudes* of these long changes in the Indian, Australian, and South American regions. If for instance the difference between the readings of the several maxima and minima of the curves plotted for Bombay and Madras be determined, it is found that they are 0·026 and 0·026 inch respectively, the mean of which is 0·026 inch. For Adelaide, Melbourne, and Sydney the differences for each are 0·054, 0·043, and 0·058 inch respectively, the mean of these three being 0·052 inch.

The actual values from which the above figures have been derived are given in the following tables, but since in this instance the points on the

Bombay.

Year.	Minima.	Mean.
	inches.	
1861—62	29·789	
1871—72	29·797	
1893—94	29·805	29·797
	Maxima.	
1875—76	29·821	
1886—87	29·824	
1900—01	29·823	29·823
Difference ...	...	0·026

Madras.

Year.	Minima.	Mean.
	inches.	
1848—49	29·808	
1861—62	29·808	
1870—71	29·804	29·807
	Maxima.	
1856—57	29·832	
1865—66	29·837	
1876—77	29·830	29·833
Difference ...	...	0·026

General mean difference 0·026 inch.

Adelaide.

Year.	Minima.	Mean.
	inches.	
1861—62	30·023	
1870—71	30·035	30·029
	Maxima.	
1877—78	30·082	
1886—87	30·093	
1895—96	30·073	30·083
Difference ...	...	0·054

Melbourne.

Year.	Minima.	Mean.
	inches.	
1862—63	29·914	
1873—74	29·921	
1893—94	29·915	29·917
	Maxima.	
1867—68	29·947	
1886—87	29·973	29·960
Difference ...	...	0·043

Sydney.

Year.	Minima.	Mean.
	inches.	
1862—63	29·842	
1874—75	29·829	
1880—81	29·837	29·836
	Maxima.	
1857—58	29·896	
1886—87	29·902	
1895—96	29·883	29·894
Difference ...	...	0·058

General mean difference 0·052 inch.

curve are derived from means of four years, the years given refer to the two middle years of each four.

In the case of Australia then this long variation has an amplitude *twice as large* as that of India, a feature which I think has not been pointed out previously. The magnitude of the amplitude of this long barometric swing must have a great effect in changes in Australian weather, and most probably is responsible for the marked secular weather changes which have been previously shown to exist in this region of the world.

To determine the amplitude of the oscillation in South America, differences between the readings of the maxima and minima points on the four-year mean curves were also determined. The mean of the values for Cordoba (0·032 inch), Santiago (0·045 inch), and San Juan (Buenos Ayres) (0·039 inch) was 0·039 inch.

This value is intermediate between the Indian (0·026 inch) and the Australian (0·052 inch) amplitudes.

The values for the individual stations were as follows:—

Cordoba.

Year.	Minima.	Mean.
	inches.	
1881—82	28·499	
1900—01	28·492	28·495
	Maxima.	
1875—76	28·521	
1893—94	28·524	28·527
Difference ...	...	0·032

Santiago.

Year.	Minima.	Mean.
	inches.	
1876—77	28·215	
1900—01	28·192	28·203
	Maxima.	
1872—73	28·252	
1893—94	28·244	28·248
Difference ...	...	0·045

San Juan (Buenos Ayres).

Year.	Minima.	Mean.
	inches.	
1881—82	29·911	
1887—88	29·909	29·910
	Maxima.	
1873—74	29·949	29·949
Difference ...	...	0·039

General mean difference 0·039 inch.

It may be of interest here to summarise in tabular form the amplitudes of the mean annual and the short and long variations of barometric pressure for the stations used in this enquiry which have been found to be most conspicuous. Two columns of figures, the third and last, indicate the *percentages* of the amplitudes of the short and long changes in terms of the mean annual variations determined from a long series of years in each case:—

Amplitudes of Pressure Variations.

Stations.	Mean annual variation.	Short variation.	Percentage of annual.	Long variation.	Percentage of annual.
Bombay	0·283	0·033	11·7	0·026	9·2
Madras	0·297	0·036	12·1	0·026	8·8
Adelaide	0·226	0·077	34·0	0·054	23·1
Melbourne	0·204	0·076	37·2	0·043	21·1
Sydney	0·212	0·071	33·0	0·058	27·3
Cordoba	0·177	0·037	20·9	0·032	18·1
Curityba	0·188	0·028	14·9	—	—
Goya	0·248	0·038	15·3	—	—
San Juan (Buenos Ayres)	0·236	0·046	19·5	0·039	16·5
Santiago	0·128	0·042	32·7	0·045	35·1

The values shown in this table are very striking. In the case of Australia, for example, the fact is made apparent that the amplitude of the variation of short duration amounts in the mean to as much as 35 per cent. of that of the mean annual variation, while that of the variation extending over about 19 years reaches nearly 25 per cent. Considering the great magnitudes of these changes in relation to those of the mean annual variations, no doubt can remain as to the important *rôle* which must be played by them in bringing about changes in the seasons from year to year.

In a previous paragraph it has been mentioned that the amplitudes of the variation of short duration, expressed in percentage of the annual swing, suffers a change on account of the position of the stations as regards latitude. To illustrate this for the region including India and Ceylon, the pressure observations at several stations have been analysed, and the result is given in the following table. The stations are arranged in order of latitude, so that the increase in latitude will be seen to correspond generally with a decrease in the values of the percentages mentioned above:—

—	Lat. N.	Mean annual variation.	Short variation.	Percentage.
	° ′	inch.	inch.	
Colombo	6 56	0·094	0·027	28·7
Coimbatore	11 0	0·200	0·036	18·0
Madras	13 4	0·297	0·036	12·1
Bombay	18 54	0·283	0·033	11·7
Nagpur	21 9	0·436	0·036	8·3
Allahabad	25 26	0·555	0·031	5·6
Jaipur	26 55	0·498	0·025	5·0
Jacobabad	28 24	0·647	0·031	4·8
Lahore	31 34	0·574	0·039	6·7
D. Ismail Khan	32 0	0·620	0·040	6·4

This percentage change is not so much due to the variation of the amplitude of the change of short duration as to the increase with the latitude of that of the mean annual variation as shown in the second column of figures above.

The question now arises: how does the long South American variation compare with those shown to exist in the Indian and Australian areas?

In the first instance it will at once be seen that the South American curve is of a type conforming more, in length of swing, to the Australian variation than to that in India. Further, there is no doubt about the *non-coincidence* of the principal epochs.

In order to make a closer comparative study of these variations, hypothetical curves embodying the main features of these changes have been drawn at the bottom of each of these two series of curves illustrated in Plates 2 and 3. These are intended to indicate in *single* curves the *general nature* of the variations as regards their epochs of maxima and minima.

In Plate 2 the epochs of the two principal maxima for the Australian area are seen to occur at about 1868 and 1887, while three subsidiary maxima are suggested at about the years (1858 ?) 1878 and (1898 ?), but the epochs of the first and last of these are very uncertain, as the curves do not extend over a sufficiently long period of time. Nevertheless, it may here be

remarked that the interval between the two chief maxima is 19 years, while those between the successive secondary maxima are about the same length.

Forming a hypothetical curve in exactly the same way for the South American region (see Plate 3), the two principal maxima here fall in the years 1874 and 1893, while a subsidiary maximum occurs somewhere between 1880 and 1885. Here again the interval between the two main maxima is 19 years.

In both of the hypothetical curves those portions representing the fall from and the rise to a principal maximum have been connected by a dotted line as if a subsidiary maximum did not exist, thus forming a principal (but really non-existent) minimum.

The object of doing this is to indicate that in the Australian area the rise to the principal maxima seems to be more abrupt than the fall from them, while in the South American area *the opposite* feature seems to be the case. An unsymmetrical curve seemed in both cases to represent the main features better than one drawn symmetrically. In fact, in the Australian area there is suggested an 8-year rise and an 11-year fall, while in the South American region an 11-year rise and an 8-year fall is indicated.

Particular attention is called to this unsymmetrical peculiarity of the curves, since a similar feature was found to be present in the curve representing the barometric variation of about four years' duration,* in operation in India and Cordoba. It was there stated that for Cordoba "the points of maxima of the hypothetical curve at the top of the plate do not lie midway between the minima on either side of them, but nearer the preceding minimum."

In order to be able to make a direct comparison between these two hypothetical curves representing the barometric changes of long duration in the Australian and South American areas Plate 4 has been added. In this the South American curve is placed directly above that for Australia, and below the latter is given the South American curve *inverted*.

The first striking fact which this comparison indicates is the remarkable similarity of the nature of the variation in the two cases. Both curves seem to have principal maxima occurring at intervals of about 19 years, while situated between these is another maximum of a subsidiary nature.

The second point of importance is that the epochs of these maxima in these two areas *are not coincident*. Further, we are not here in the presence of a barometric see-saw, or opposite pressure variation, because the Australian maxima do not occur simultaneously with the South American minima; there seems to be a general time difference of phase amounting to about

* 'Roy. Soc. Proc.,' vol. 76, A, p. 503, 1905.—Note.

six years, the epochs of the Australian high pressures preceding those of the South American region.

In the case of the barometric variations of short duration existing between India and South America, the inversion of the latter curve corresponded exactly with the direct curve of the former. In order to make a similar comparison, the South American curve representing the curve of long duration has here also been inverted and it will be observed that the curves are not the inverse of each other.

The above discussion of barometric changes occurring over large areas shows, I think, clearly that the *type* of variation taking place in South America is closely similar to that existent in Australia, but unlike that in operation in the Indian area.

With so short a length of time covered by the observations it is difficult to say, especially with regard to Australia, whether the recurrence of the maxima and minima is of a regular periodic nature or not. Judging by the curves and figures which have been referred to in this paper, there seems to be a general indication that the intervals between the maxima or minima in the case of India are, on the average, approximately 11 years in length, while in the case of the Australian and South American regions the principal maxima are 19 years apart.

I have previously indicated that the Australian pressure change of long duration is undoubtedly very closely associated with that in India, but that the reduction of the intensity of the maximum about the year 1877 in most of the Australian stations alters very considerably the aspect of the Australian curves.

It seems, therefore, probable that if a satisfactory cause be found which is producing the fluctuations in one of these areas, then those in the other area will be subject to the same influence, but will be modified by some cause due possibly to a different geographical position.

In comparing such regions as India and Australia it is as well, in this connection, to bear in mind the continental condition of the former and the insular condition of the latter, each of which has its own special effects on meteorological changes.

In looking for the cause of these barometric changes which extend over several years, it seems as if the solar changes, as exhibited by the frequency or areas of sun-spots (the only indication of solar activity extending over a long period of time that exists), are responsible for the Indian fluctuations. To indicate this relationship the sun-spot curve (inverted) is placed at the top of Plate 2. This curve represents the variation from year to year of the mean daily areas of sun-spots deduced from both hemispheres of the sun.

Perhaps different solar data handled in another manner might indicate a closer relationship than is at present suggested.

Although the existing relationship may be considered of too approximate a character to indicate clearly a cause and effect, there is undoubtedly a general similarity between the sun-spot variation curve and that representing barometric changes in India from 1844 to 1903, a period of 59 years. Years of average high pressure are years of few sun-spots, and *vice versâ*, but there is a marked exception to this about the epoch of sun-spot maximum in 1883, which maximum, it may be remarked, was much smaller in intensity than those of 1870 and 1860.

If India be thus dominated by the solar changes, then the curves for Australia and South America become of secondary importance from the solar point of view and may be considered as a modification of the Indian variation, due possibly to some terrestrial cause. How this modification is brought about I am not yet prepared to say, but I do not think we need be driven to explain the Australian or the South American barometric changes as depending either on lunar influence or a solar variation of about 19 years.

The similarity of the curves representing the pressure changes in India and the sun-spot curve is not pointed out here for the first time. In fact, so striking was the resemblance between curves representing these changes in years previous to 1880 that the attention of several meteorologists was drawn to the close association of these two phenomena.

Thus F. Chambers, writing in 1878,* concluded that the curves "support each other in showing a low pressure about the time of sun-spot maximum and a high pressure at the time of sun-spot minimum." He further stated:—

"The range of the variation of the year by mean pressure from the minimum of 1862 to the maximum of 1868 is 0·042 inch and the mean range of the barometer from January to July is 0·291 inch, from which it appears that the variation of pressure produced by the absolute variations of the sun's heat are, in comparison with the usual seasonal changes, by no means insignificant."

J. A. Brown,† S. A. Hill,‡ Sir John Eliot,§ H. F. Blanford,‖ E. Douglas Archibald¶ and others have all corroborated in a general manner this relationship between pressure change and sun-spot variation; Douglas

* 'Nature,' vol. 18, p. 568.
† 'Nature,' vol. 19, p. 7, 1878.
‡ 'Nature,' vol. 19, p. 432, 1878.
§ 'Indian Meteorological Reports,' p. 170, 1877.
‖ 'Nature,' vol. 21, p. 479, 1880.
¶ 'Indian Meteorological Memoirs,' vol. 9, p. 543, 1897.

Archibald used data which extended up to the year 1893 and his deductions, which I think are the most recent, were:—

"The mean anomalies present all the characteristics of a true period, rising to a maximum of 0·0132 inch about the epoch of minimum sun-spot, and, with an exception in the sixth year, falling to a minimum of 0·0100 inch coincidently with that of maximum sun-spot, the former barometric epoch slightly preceding, and the latter slightly following the corresponding solar epoch as is usual in all other sun-spot comparisons . . ."

"Still the figures from the other years, and the repetition in each cycle, show that there is a cyclical tendency to high pressure at the time of few spots and low pressure at the time of many spots . . . the amplitude of the variation amounts to 0·02 inch . . ."

By utilising in this inquiry observations made up to the most recent date possible, 1905, it will be seen (Plate 2) that the sun-spot maximum of 1893 corresponded with an epoch of mean low pressure about that epoch; while up to 1901, a year of about sun-spot minimum, the pressure had steadily risen. It is thus evident that the same relationship is still in operation, only the amplitude is much smaller than was the case in the earlier years of observation

So far as I am aware, the long *barometric* swing of 19 years in Australia has not been pointed out before (Brückner omitted the Australian area in his pressure investigation*) but the existence of a 19-year period of rainfall change has often been mentioned.

One of, if not the earliest record of it is in "Notes on the Climate of New South Wales," 1870, by Mr. H. C. Russell, and in a later paper which he published in 1876,† he more strongly advocated this rainfall cycle.

In a still later paper which he published in 1896,‡ Mr. Russell collected information of a miscellaneous kind and extended his 19-year rainfall cycle both over a greater period of time and a wider area. In fact Australia, India, Europe, Asia, Africa, North and South America, all tended to give him general ideas relating to droughts, which he marshalled and from which he deduced that this cycle was occurring over the whole earth, epoch for epoch, nearly simultaneously. Mr. Russell was finally led to give up the idea of the sun-spot cycle as influencing rainfall.

In place of solar action he regarded the moon as the origin of this cycle, a suggestion which he made in 1870§ and again in 1896.‖

* 'Klimaschwankungen seit 1700,' Eduard Brückner, p. 194, 1890.

† 'Journal of the Royal Society of New South Wales,' vol. 10, p. 151, 1876.

‡ 'Journal of the Royal Society of New South Wales,' vol. 30, p. 70, 1896.

§ 'Notes on the Climate of New South Wales,' 1870.

‖ 'Journal of the Royal Society of New South Wales,' vol. 30, p. 90, 1896.

It may, in conclusion, be stated that while the present investigation fully endorses the results of Indian meteorologists as regards the relationship between pressure and sun-spot variation, and agrees with regard to length of period with Mr. Russell's long period cycle in Australia (so far as the observations since 1857 permit), it does not corroborate his view that this cycle is world-wide in extent, with similar epochs of occurrence of the maxima and minima, or is dependent necessarily on lunar influence.

On the completion of this paper I took the opportunity of submitting it to Dr. W. N. Shaw, F.R.S., and I should like here to express my thanks to him for kindly reading it through and making valuable suggestions. Owing to the shortness of the time covered by the observations discussed in this paper I refrained from entering into any of the possible barometric changes which were visible in the curves other than those to which mention has already been made.

Dr. Shaw suggested, however, that as I had eliminated the variation of about four years' duration to render apparent the changes of 11 and 19 years, I should proceed a step further and eliminate the 11-year change from the curves, since both the Indian and Australian pressure values exhibited changes of about this length. The object of this procedure was to find out whether the 19-year variation was a possible harmonic of the 4- and 11-year changes or a separate variation independent of these two shorter oscillations. If the former, then it should be absent after the observations had been freed from these two variations.

To accomplish this, 11-year mean values were formed, that is, the value for each year plotted was composed of the combined mean for that year with the addition of the five years each side of this date. Such an operation not only eliminates any periodic change of 11 years, but at the same time disposes of the variation covering about 4 years.

Plate 5 shows the resulting curves for India, East Indies, and Australia after the above-mentioned treatment. The South American would have been similarly handled if the series of observations at each station (excepting Santiago) had been longer.

An examination of these curves shows that distinct variations still remain, and they are most marked in the Australian area, being specially prominent in the curve for Sydney and a little less so in that for Melbourne. The variation at Adelaide is almost as strong as at Sydney, but, as before in the case of the 11-year change, is not quite of the same nature. At Bombay a variation of much longer duration seems to be in operation, while the curve for Madras suggests maxima about 19 years apart, which in this respect conform with those of the Sydney curve; the amplitude, however, is very

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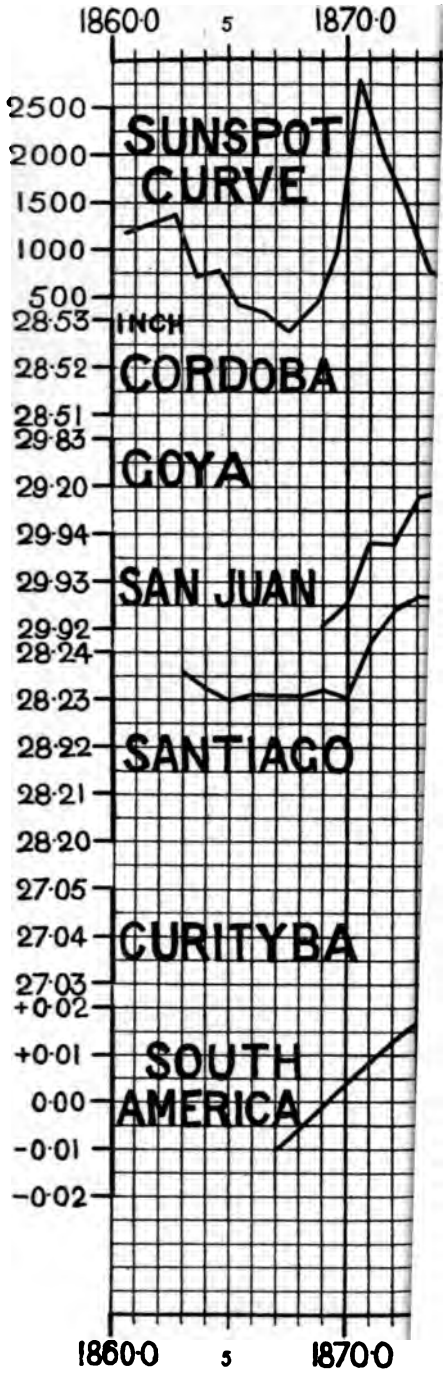

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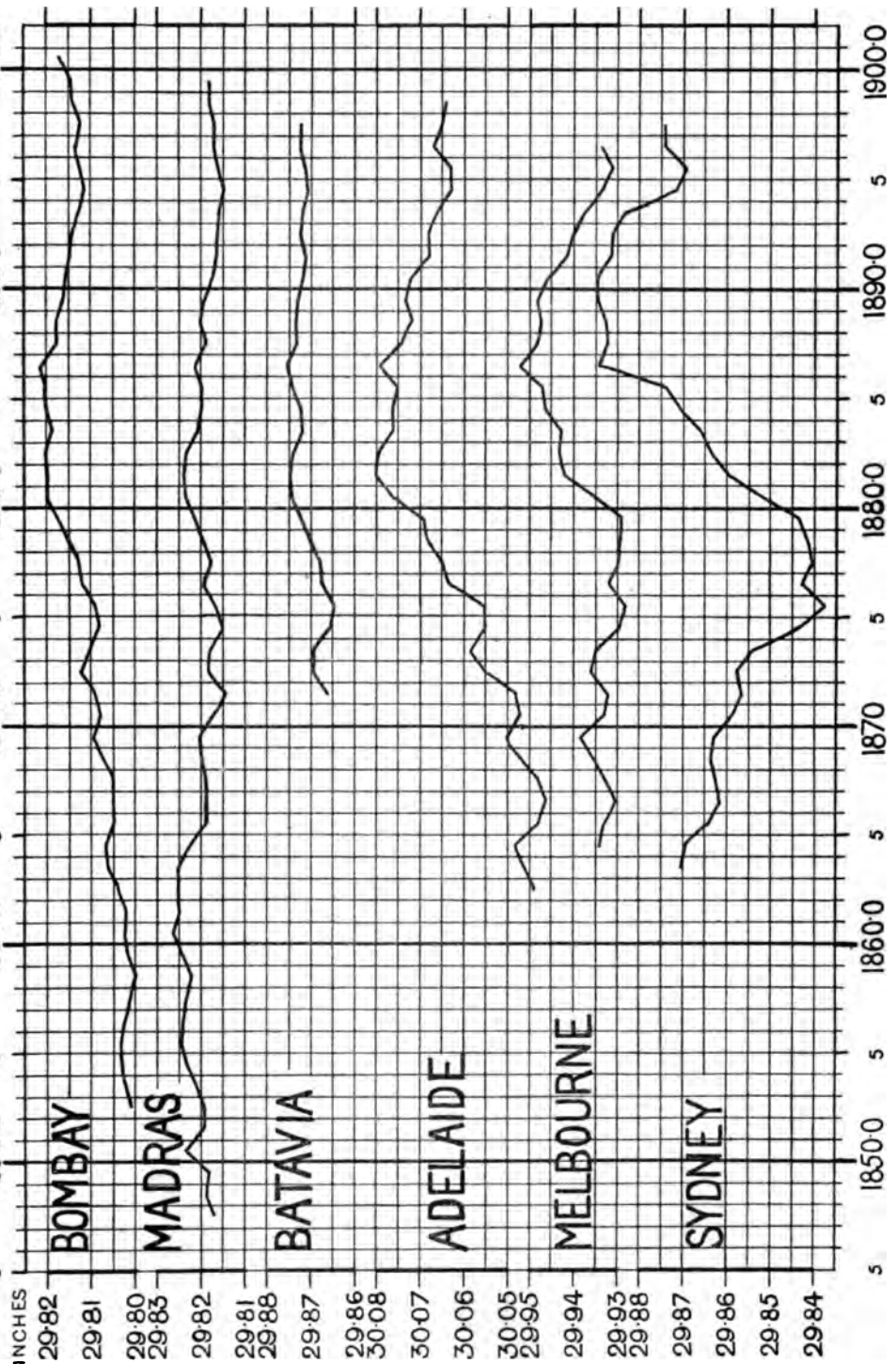


Curves to illustrate the Pressure Changes in India and Australia after the Elimination of the 4- and 11*-year Variations.*

much less. The observations at Calcutta have been treated in a similar manner, but the resultant curve seems to represent a variation which differs from both those of Bombay or Madras.

The time dealt with in these curves is, however, so short that any reference to the possible periodic nature of these curves for the present is out of the question. The variations exhibited are, however, very suggestive, and when further observations have been accumulated, a more definite idea of these barometric changes will be gleaned.

I take this opportunity to express my thanks to the Director of the Solar Physics Observatory, Sir Norman Lockyer, for permitting me to prepare this paper for the Society. I am indebted also to Messrs. W. Moss and T. F. Connolly, computers in the observatory, for the abstraction, reduction, and drawing of the curves of the observations.

Conclusions.

Summing up the results arrived at regarding the behaviour of the curves representing these long barometric changes, it may be stated:—

1. The Indian variation is nearly the inverse of the 11-year (about) sun-spot cycle, that is, years of mean high pressure are generally those of small spotted area.

2. The Australian variation is allied to, but in part a modification of, the Indian variation.

3. The interval between the Australian *principal* maxima is about 19 years.

4. The interval between the South American *principal* maxima is about 19 years.

5. The South American variation is not the inverse of that of Australia, but there is a time-phase difference between the maxima of about six years, the Australian maxima preceding those of South America.

6. There seems evidence to suggest that the 19-year variation is due to solar action modified by some terrestrial cause.

7. So far as the research has gone, no explanation has been found of the cause of the modification of the prominent 11-year variation in India into those of the pronounced 19-year changes which occur both in the Australian and South American regions.

[*Addendum, June* 8, 1906.—Since this communication was sent to the Royal Society I find a still earlier reference to the 19-year cycle in Australia. In an article on the "Development of Meteorology in Australia," by Mr. Andrew Noble, of the Sydney Observatory, it is stated—"Australian meteorology is greatly indebted to the Rev. W. B. Clarke for his untiring

efforts in its behalf during those early years, beginning with his observations at Paramatta in the year 1839 and continuing long after the inauguration of the New South Wales service under Government auspices in the year 1858. . . . The 19-year cycle theory, elaborated by Mr. Russell in more recent years, was advanced by Mr. Clarke in the 'Sydney Morning Herald' of May 1, 1846."* This reference is of great interest, since it indicates that this 19-year variation was evidently quite a prominent feature of Australian weather *before the observations* discussed in the present communication were made.]

The Transition from the Liquid to the Solid State and the Foam-Structure of Matter.

By G. QUINCKE, For.Mem.R.S., Professor of Physics in the University of Heidelberg.

(Received June 6,—Read June 21, 1906.)

1. On June 19, 1905, I laid before the Royal Society the results of my researches on ice-formation and glacier-grains. The further prosecution of these researches has shown that phenomena similar to those observed in the freezing of water occur in all bodies in nature, and are in agreement with the structure of metals as observed by myself and also by other investigators, who in some cases have described their results in the 'Philosophical Transactions.' Solid bodies, then, are never homogeneous, but always exhibit a foam-structure.

2. For brevity's sake I use the word "oily" to describe any liquid that tends to make its surface as small as possible, and exhibits surface tension at the boundary separating it from another liquid.

All liquids in nature resemble water in forming, as they cool, oily foam walls, which may be very thin and invisible. The shape and position of these foam walls become visible on freezing or thawing in the following ways:—

(*a*) By fissures or fractures at the surface of the foam walls, whenever the liquid contents of the foam cells contracted on solidification, or when the walls and the contents of the foam cells contracted differently as they cooled.

* 'Monthly Weather Review,' vol. 33, No. 11, November, 1905, p. 480. Washington, U.S.A., Weather Bureau.

(*b*) By the bounding surfaces of the doubly refracting crystals (glacier-grains) which are differently orientated in neighbouring foam cells.

(*c*) On illumination with sunlight or electric light, or on warming, when the doubly refracting contents of the foam cells melt and are transformed into singly refracting liquid.

(*d*) By lens-shaped masses, foam flakes or air bubbles, suspended in the foam walls.

(*e*) By the furrows, or network of lines on the solidified surface formed by the intersection with that surface of the foam walls in the interior of the solidified mass.

(*f*) By polishing or etching the natural or artificial surface, in cases when the walls and the contents of the foam cells differ in hardness, or in the rapidity with which they are attacked by chemical reagents.

3. Pure *benzene*, slowly frozen in glass flasks, shows foam walls and fissures (normal to the glass surface) inclined to one another at 120°. The totally reflecting planes in the interior bound foam cells (glacier-grains) or hexagonal tables, each of which contains a crystal, differently orientated in the different foam cells. In the case of quickly frozen benzene, the foam walls are often warped or twisted, and the bounding surfaces of the benzene-grains exhibit waves, folds, or furrows, or parallel fibres. The light from an arc lamp developed in the clear contents of the separate foam cells a row of parallel bands of "dendrites," or fir-tree formations, the needles of which changed in daylight into tubes with rounded heads and totally reflecting walls, and swelled up. The tubes formed bulbous enlargements and fell into strings of bubbles, some rounded, and some elongated.

Benzene, slowly frozen in a rectangular glass trough, appeared clear between the white diagonal planes, which had frozen last and contained rounded air bubbles. Illumination for a few seconds with the arc light developed in the clear benzene fine dividing walls (normal to the surface) which bounded hexagonal prisms, 3 mm. wide and 8 mm. long. Beneath the sides of the prisms the solid benzene surface showed, on illumination, furrows like those of an ice-block exposed to radiation, corresponding in fact to Forel's bands in glacier ice. Pressure with a steel point caused the solid block of benzene to cleave along the diagonal planes with a fibrous fracture, the fibres being normal to the surface, just as in an ice-block.

The phenomena presented by benzene and water when freezing and thawing are extraordinarily similar. The air-filled tubes in the diagonal planes are, in the case of water, thinner and more numerous than in benzene, which contains more spherical air bubbles. Water is thus more viscous while solidifying than is benzene.

There is an essential difference between water and benzene in the fact that, on freezing, water expands, whereas benzene contracts. In the case of benzene, therefore, the walls of the foam cells become visible through the totally reflecting surfaces between the glacier-grains.

4. *Water, benzene, acetic acid and glycerine,* when exposed in the form of clear solid blocks to the electric light, exhibit liquefaction figures of various shapes at the places where, as the cooling proceeded, traces of impurities had separated out at periodic intervals. These correspond to the liquefaction figures observed by Tyndall in natural ice.

5. *Bromine,* frozen in a test tube and illuminated with the arc light, showed on the surface a network of fine furrows inclined to one another at 120°, and in the interior totally reflecting fissures (normal to the surface) at the places which had been occupied by invisible layers enclosing hexagonal prisms 2 to 3 mm. long.

6. *Red hæmatite* has a surface like a mass of soap bubbles, and is bounded by spherical surfaces 10 mm. in diameter, in which are distributed small lens-shaped masses, 0·2 mm. in size. The spherical surfaces cut at angles of 120°, 90°, and so on, and are inclined at 120° to the cleavage planes that terminate in the lines of intersection of these spherical surfaces. On these cleavage planes can be distinguished fibres normal to the surface, as in melting ice. In the outer, quickly solidified layers, the fibres are 0·06 mm. thick, but in the interior, where the solidification occurred more slowly, they are 0·36 mm. thick, thus resembling the fibrous foam cells in quickly and slowly frozen ice.

7. *Malachite* and *chalcedony* exhibit forms similar to those of red hæmatite, save that there are no lens-shaped masses in the spherical surfaces.

8. The light-coloured veins that traverse the darker ground mass of *marble* and *sandstone* are twisted screw-surfaces, conical tubes swollen out at some places, pinched in at others, and spirally twisted, in the walls of which are distributed hollow lens-shaped spaces and smaller foam cells. These veins exhibit, therefore, the forms assumed by an oily viscous liquid under the influence of its surface tension.

9. Pure *molten salts*—NaCl, KCl, KBr, KI, Na_2CO_3, Na_2SO_4, $Na_2B_4O_7$—when dropped on to platinum foil and allowed to solidify, show, like solidified benzene, many totally reflecting fissures, or plane layers, 0·05 to 0·25 mm. wide, which are bounded by straight lines or arcs of circles, and are inclined to one another at 120° or other angles. These plane layers, as the cooling proceeded, had contracted differently from the contents of the foam cells enclosed by them. In the surface of these layers or foam walls there lay lens-shaped masses, 0·01 to 0·02 mm. in size, arranged singly or in

two intersecting rows of 8 or 10 each. Sometimes these intersecting rows have the same orientation in several neighbouring foam walls (totally reflecting surfaces).

Molten Na_2SO_4 showed zig-zag fissures normal to the surface, and inclined at 120°. In the corners of the zig-zags three oily layers had met. The thinnest invisible layer had had, it is true, the same surface tension as the two others, but the tension caused by the thermal contraction had been insufficient to produce a fissure.

In freshly melted drops of Na_2CO_3 there were foam walls, normal to the surface and inclined at 120° to one another, which bounded hexagonal prisms. At the points of intersection of the edges of the foam walls there lay occasionally, as in the case of thawing ice, a tetrahedron bounded by spherical surfaces.

10. The surfaces of solidified drops of pure molten *metals*—such as I used in 1868 and 1897 for measuring the surface tension of these metals—show a network of straight lines or arcs of circles (usually inclined to one another at 120° or 90°), or foam walls with embedded lens-shaped masses. This is so in the case of gold, silver, platinum, palladium, iridium, indium, copper, zinc, iron, nickel, cobalt, bismuth, sodium, kalium, mercury. Similar phenomena are to be observed on the surface of solidified drops of sulphur and selenium, or on the surface of carbon which has been distilled with the electric arc in a magnetic field, and deposited on the cathode.

The more quickly a metal has solidified, the smaller are its foam cells.

11. On account of the volume changes which occur when metals solidify, the shapes and mutual inclinations of the foam cells are somewhat deformed.

12. Ewing and Rosenhain (1900 and 1901), and Osmond and Cartaud (1901) have published fine photographs of the *surfaces of metals solidified on glass*. In the case of lead these photographs show metallic grains or hexagonal foam cells with angles of 120°, and, near the edge, of 90°. The foam walls are identical in shape and inclination with the 300 times larger foam walls which I saw forming in the median plane of a slowly thawing prism of ice. Parallel cylindrical tubes, already partially transformed into strings of spheres, can be followed through many neighbouring foam cells, just as in ice. The tubes and strings had therefore been formed before the walls of the hexagonal foam cells.

Hexagonal foam cells similar to those in lead, together with rounded lens-shaped masses in the middle of the foam cells, are visible in the photographs of the solidified surfaces of tin and zinc. On the surface of a zinc drop can be recognised radially-arranged straight and twisted fibres, with

swellings, and foam cells inside, as in a sphero-crystal. Many of these fibres have already fallen into rows of spheres.

In Ewing and Rosenhain's photographs of cadmium castings on glass, one recognises a network of straight lines and arcs of circles (mostly with mutual inclinations of 120°) which bound metallic grains or foam cells 0·02 to 0·07 mm. in size, and have gas bubbles at the boundaries of the foam cells. The metallic grains easily suffered mutual displacement. The surfaces at which such displacement or slipping took place were thus the walls or bounding surfaces of the foam cells, precisely as in the case of the glacier-grains of ice.

Molten tin formed smaller foam cells the more quickly it had been cooled.

The metallic grains of cadmium and lead grew larger at temperatures below the melting points of the metals. In my opinion this enlargement occurred, as with the glacier-grains of ice below 0°, by the bursting of some of the foam walls, and the running together of the contents of the foam cells.

Holborn and Henning (1902) experimented with *thin strips of* iridium, rhodium, platinum, palladium, gold and silver *foil*, which they *heated nearly to melting point* by means of an electric current. They obtained on both sides of such strips the same network of straight lines and arcs of circles inclined at 120°, but often also at other angles.

In the network of lines there are also frequently to be recognised closed circles, 0·02 to 0·1 mm. in diameter, containing rows of very small lens-shaped objects or bubbles.

Thin strips of electro-iron were heated *in vacuo* by Sir W. Roberts-Austen (1896) to a temperature of 1500° by means of an electric current, and carbonised with diamond, starting from one end. Osmond's photograph of this strip shows linear and curved foam walls, 0·001 to 0·005 mm. thick, inclined at 120°, and enclosing dark foam cells 0·08 mm. across.

13. The shapes of the bounding surfaces of molten metals, and the circular arcs in the network of lines on the surface of metals raised to red or white heat prove, in my opinion, that these bounding surfaces must be regarded, not as they have hitherto been, viz., as crystalline faces, but as solidified oily foam walls, which, as in the glacier-grains of ice, enclose foam cells with contents differing from the walls. Just as the glacier-grains of ice run together and enlarge by the bursting of the foam walls, so also larger foam cells with fewer foam walls are formed in metals heated nearly to melting point.

14. The electrically heated metal appears softer, because of the lack of the foam walls, whose surface and surface tension increase the rigidity of the metal, as I proved in 1868.

15. A network of lines or foam walls similar to that on the natural surface of solidified metals comes to light also on *artificial surfaces of metal* castings when these are polished, or suitably etched by acids or other liquids. The foam walls are attacked or dissolved either more easily or less easily than the contents of the foam cells. If the foam walls are not normal to the artificially produced surfaces, then, of course, the mutual inclinations of the lines on these surfaces are different from those of the foam walls.

16. Sorby, A. Martens, Osmond and Werth, Osmond and Sir W. Roberts-Austen, Osmond and Cartaud, Th. Andrews, Ewing and Rosenhain, Beilby, Humfrey, E. Heyn, and C. Benedicks have given drawings of these networks of lines and etched figures for iron and steel, gold, platinum and lead. In general the etched figures of the artificial surface correspond to the network of furrows on the natural surface of the same metal.

Figures of sections parallel and perpendicular to natural cleavage planes of the crystals of spiegeleisen, given by A. Martens, show parallel tubes, which lie parallel to the cleavage plane and fall into separate drops. Often there are visible two intersecting systems of parallel tubes (which show bulgings, or are resolved into strings of drops), or "fir-trees" with branches normal to the main trunk. These branches show several bulgings and rounded heads, occasionally having in their interior spheres lying side by side, transverse walls and foam masses. At times the branches of the "fir-trees" also fall into separate spheres. There are also cracks 0·04 mm. wide, normal to which lie numerous parallel layers or fibres, as in ice. This structure has since been named perlite.

Breakage surfaces, and ground and etched surfaces of Bessemer steel exhibit, in the figures given by Martens and by Osmond and Werth, straight and twisted fibres normal to the surface. Steel gives breakage surfaces showing folds, and wave-like and zig-zag markings. On the crystal faces of spiegeleisen there lie dendrites.

Heyn has photographed etched surfaces of slowly cooled iron containing varying amounts of carbon. Iron with 0·05 per cent. of carbon shows fine circular foam walls of carbide of iron, Fe_3C (cementite), which enclose foam cells 0·04 to 0·1 mm. in diameter, filled with iron (ferrite), and meet at angles of 120°, 90° and so on. In the partly invisible foam walls are suspended islets of perlite. In the case of iron containing more carbon, the carbide of iron separated periodically in parallel layers, or as parallel cylindrical tubes with bulgings and rounded heads, or as spherical foam walls enclosing "foam lenses" and foam cells, 0·001 to 0·003 mm. in diameter. The tubes, lenses and foam cells are filled with iron, and surrounded by iron. The greater the percentage of carbon, and the more quickly the molten iron is

cooled, the less is the distance of the layers from one another and the smaller are the foam cells, just as in the case of ice containing any salt.

The shapes of the microscopic structures in solidified iron containing carbon are the same as in ice containing salt. The carbide of iron corresponds to the oily salt solution in freezing water.

Other foreign substances in iron—carbon in the form of graphite and temper-carbon, silicon, phosphorus, sulphur, air or other gases, and other metals such as manganese and nickel—even if present only in small quantities are able (like the traces of salts in ice) considerably to modify the surface tension, melting point, and viscosity of the foam walls and of the contents of the foam cells, and the size and shape of the foam cells or glacier grains of the iron.

In quickly cooled steel the etched surfaces figured by C. Benedicks show fissures on the circumference of spirally twisted conical tubes.

17. Pure molten metals after solidification exhibit on artificial polished and etched surfaces a network of lines or foam cells (similar to the glacier-grains of ice), which are bounded by thin foam walls. These thin foam walls themselves contain still smaller foam cells, as is proved by the visible lens-shaped masses embedded in them, and the wave-like furrows on their surface, which are capable in reflected light of giving diffraction colours like mother-of-pearl.

This foam structure of pure metals when solidified after fusion has been demonstrated in the case of:—

Bismuth	Iridium	Platinum
Cadmium	Lead	Potassium
Cobalt	Manganese	Rhodium
Copper	Mercury	Sodium
Gold	Nickel	Tin
Iron	Palladium	Zinc
Indium		

18. Molten metals solidify on cooling to a liquid jelly, and later to a solid jelly. The walls and contents of the foam cells of such a jelly still consist of viscous liquid, *i.e.*, the jelly itself is still liquid—like ice—at temperatures lower than the melting points of the respective metals. The welding of two pieces of metal corresponds to the running together of the cell walls and cell contents of two lumps of jelly, or the regelation of ice.

19. All the other substances in nature behave like these metals. The soft, plastic condition, which all bodies assume for a larger or smaller interval of temperature on the transition from the solid to the liquid state,

proves the presence of jelly, *i.e.*, of oily, visible or invisible foam walls, over this interval of temperature.

20. Presumably all liquids on cooling form, before they pass into soft jelly with continuous oily foam walls, a turbid solution containing visible and invisible spheres, bubbles and foam flakes of oily, half-solidified substance, suspended side by side.

21. The heterogeneous oily liquid, which as solidification occurs becomes visible in all substances in nature in the form of thin foam walls of different surface tension, must also appear as a thin liquid skin on the surface of solidifying drops. This explains the variations in the measurements of the surface tension of molten metals and salts, and of liquids in general.

22. The walls and contents of the foam cells consist of heterogeneous substance. That foreign matter in very small quantities—1/1000000 per cent. and even less—does form oily layers and foam walls in pure liquids, is proved by my observations on ice and benzene. Traces of foreign matter (gases, carbon, metals, etc.) too small to be shown in any other way are present even in the purest liquids, and are sufficient to explain the observed foam structure of all solidified substances in nature.

23. As however in every liquid, even the purest, the number of the foam cells increases and their size diminishes as the velocity of cooling and solidification increases, it is in my opinion necessary to assume that, even in perfectly pure liquids, oily heterogeneous liquid can separate out on cooling. Every liquid, before it solidifies, becomes for a longer or shorter time a turbid solution. A liquid does not possess constant and unchangeable properties at the same temperature and pressure. All liquids in nature form allotropic modifications, such as have long been known in the case of sulphur, phosphorus, iron, etc. Such an allotropic modification is formed in larger quantity, the more quickly the liquid is cooled, and exhibits surface tension at the common boundary with the original liquid.

On the Osmotic Pressures of some Concentrated Aqueous Solutions.

By the Earl of BERKELEY and E. G. J. HARTLEY.

(Communicated by W. C. D. Whetham, F.R.S. Received May 28,—Read June 7, 1906.)

(Abstract.)

This communication gives an account of measurements of osmotic pressures of aqueous solutions of cane sugar, dextrose, galactose, and mannite. The method adopted is that briefly outlined by us in Vol. 73, 'Roy. Soc. Proc.' A gradually increasing pressure is placed upon the solution (which is separated from the solvent by a semi-permeable membrane) until the solvent, which at first flows into the solution, reverses its direction and is squeezed out. The pressure, when there is no movement of the solvent, is considered to be the osmotic pressure. Owing to the difficulty of determining the exact point at which no movement takes place and for other reasons, the experiments are carried out so as to enable an observation to be made of the rate of movement of the solvent, both when the pressure on the solution is just below and when just above the turning point pressure. The osmotic pressure is deduced from these rates.

The range of pressures covered by the experiments is from 12 to 135 atmospheres.

A description is also given of the methods adopted for making the copper ferrocyanide membranes, and it is pointed out that with the best membranes, in most cases, a small quantity of solution comes through during the experiment. It is shown that even a small leak causes a considerable lowering of the observed pressure; hence the final results accepted are those where the leak was least.

Attention is drawn to the fact that the osmotic pressures of cane sugar solutions when measured directly and when calculated from their vapour pressures agree to within 3 per cent.

An Apparent Periodicity in the Yield of Wheat for Eastern England, 1885 *to* 1905.

By W. N. SHAW, Sc.D., F.R.S., Director of the Meteorological Office.

(Received May 7,—Read May 17, 1906.)

In a paper contributed to the Hann celebration volume of the *Meteorologische Zeitschrift*, I endeavoured to account for a curious relation between the yields of wheat for successive years in the eastern district of England by referring the variation to periodic components. The relation referred to will be understood from an inspection of the table of yields on p. 75, or the diagram which illustrates it. The yields for the years 1896, 1897, and so on, taken in chronological order, apparently "compensate" respectively those for 1895, 1894, and so on, taken in reversed chronological order. Each pair of years at equal intervals, one before and one after 1895—6, gives a mean value approximating very closely to 30·8 bushels per acre, the average yield for the 20 years 1885 to 1904. This relation is further illustrated by the yield for 1905, which was not ascertained when the paper referred to was written (November, 1905). The data have been issued since then by the Board of Agriculture, and the yield for 1905 comes out at 32·0 bushels per acre, which "compensates" the yield for 1886, 29·2 bushels per acre, the mean being 30·6, surprisingly near to 30·8.

The work of the paper referred to was based upon the supposition that a reversal of the kind indicated points to the yield being represented by the combination of a number of simple harmonic components, each having a node, ascending or descending, at the epoch 1895—6. At first I did not suppose that the components belonged to a harmonic series, and I tried to evaluate them by eliminating components of specified period, two years, four years, etc., by numerical process.* The simplification produced by taking the mean of consecutive years, and thus eliminating the simple periodic term of two years' period was considerable, and, in my contribution to the "Hann" volume, I dealt with the curve thus simplified. When I had selected periodic terms to give the best representation I could make of the curve of two-year means, one of the terms had a period of 11 years, and I could draw no practical distinction between the others and the harmonic components of a fundamental period of 11 years. In the result it was shown that the average yield for two consecutive years'

* I owe this method, which is very useful in dealing with complex periodic variations of unknown periodicities, to the suggestion of Professor G. Chrystal, of Edinburgh.

yield of wheat in the eastern counties of England between 1885 and 1904 was represented with remarkable fidelity by the equation

$$y = 31 + 2{\cdot}8 \sin \frac{2\pi}{11} n + 0{\cdot}4 \sin \frac{4\pi}{11} n - 1{\cdot}2 \sin \frac{6\pi}{11} n + 1{\cdot}2 \sin \frac{8\pi}{11} n,$$

where n is the number of years, counting backwards or forwards, from the point representing the mean for 1895—6.

The process of taking means of consecutive years not only eliminates the oscillation of two years' period, but it alters the amplitude and phase of all other periodic oscillations. It is also to be noted that an apparent oscillation of two years' period may correspond with a combination of the fifth and sixth terms of the harmonic series with a fundamental period of 11 years. These two terms have periods of 11/5 or 2·2 years, and 11/6 or 1·83 years respectively.

I have now extended the calculation to get, from what I will call the ascertained components of the curve of two-year means, the corresponding components of the curve of original values.

It is a matter of simple trigonometry to show that if a_1, a_2, a_3, a_4 are the amplitudes of the first four components in the original curve, a_1', a_2', a_3', a_4' the amplitudes of the components of the same periods in the curve of means for two successive years, then

$$a_1 \cos \tfrac{1}{2} \frac{2\pi}{11} = a_1', \qquad a_2 \cos \tfrac{1}{2} \frac{4\pi}{11} = a_2',$$

$$a_3 \cos \tfrac{1}{2} \frac{6\pi}{11} = a_3', \qquad a_4 \cos \tfrac{1}{2} \frac{8\pi}{11} = a_4'.$$

The phase of each component is altered by half a year, and thus the components remain concurrent in a common node if they are so in the original.

The equation to the first four components in the original curve is therefore

$$y_0 = 2{\cdot}9 \sin \frac{2\pi}{11} n + 0{\cdot}5 \sin \frac{4\pi}{11} n - 1{\cdot}8 \sin \frac{6\pi}{11} n + 2{\cdot}8 \sin \frac{8\pi}{11} n.$$

To get the values for successive years we have now to put n equal successively to $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$ . . ., on the positive and negative sides of the node, which in the actual curve is between 1895 and 1896.

These values were computed for each year and a curve of residuals plotted. It is an irregular curve, for the values are necessarily affected to some extent by accidental circumstances and the residual variations are not very large. In order to represent the residual curve I took two equal components, each having an amplitude of 1 bushel per acre for the fifth and

sixth terms of the series, and an ascending node at the epoch 1895—6. The final representation of the annual sequence of the yield of wheat for Eastern England is by a periodic variation of 11 years' period with its five harmonic components, as follows:—

Period.....	11	$\frac{11}{2}$	$\frac{11}{3}$	$\frac{11}{4}$	$\frac{11}{5}$	$\frac{11}{6}$	years.
Amplitude.....	2·9	0·5	−1·8	+2·8	+1·0	+1·0	bushels per acre.

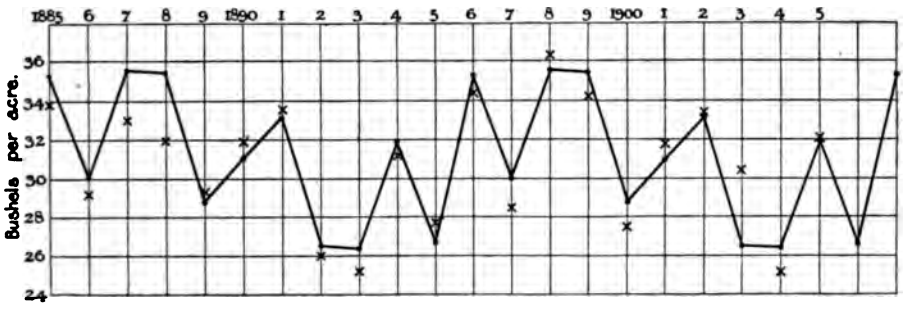
The + sign indicates that the component has an ascending node at the epoch 1895—6, the − sign a descending node. The values computed from this combination of components are shown in the table (p. 75) side by side with the actual values.

The agreement may fairly be called surprising; the differences are large for three years, 1887, 1888, and 1903, amounting in those cases to +2·7, +3·6, and −3·9 bushels respectively, but the error does not reach 2 bushels in any other year, and in 11 out of the 21 years it is less than a bushel.

When the amplitudes of the components were evaluated the yield for 1905 was unknown, the computed value was 31·9 bushels, the actual value turns out to be 32 bushels, thus showing a very striking agreement between calculation and actuality.

The relation between the computed values and the actual values is shown best by the diagram (fig. 1). It appears therefrom that the direction of the actual variation is the same as that of the computed variation for every step of consecutive years, though the amount of the variation is different to the extent indicated in what has been said above.

FIG. 1.—YIELD OF WHEAT, ENGLAND EAST, 1885—1905.



The line represents the combination of the harmonic components—

Period	11	$\frac{11}{2}$	$\frac{11}{3}$	$\frac{11}{4}$	$\frac{11}{5}$	$\frac{11}{6}$	years.
Amplitude [31]	+2·9	+0·5	−1·8	+2·8	+1·0	+1·0	bushels per acre.

Each has a node (+ascending, −descending) at 1895—6.
The crosses denote the actual yields of the several years.

The curious reversal in the variation of yield with reference to the epoch 1895—6 is thus satisfactorily accounted for by regarding the variation as the result of a simple periodic oscillation of 11 years' period with its five harmonic components of suitable amplitude.

Objection may be raised to the method adopted to obtain the amplitudes of the components. It is partly by numerical calculation and partly by trial with plotted residuals, and thus does not follow a strictly orthodox process. As a matter of fact, I was not prepared to find 11 years as the fundamental period, and the result has been extorted from me somewhat against my will by a long manipulation of the numbers having the reversal with reference to 1895—6 as the governing consideration. When I first took the matter up, although I considered the reversal to be obvious evidence of periodicity, I did not consider that I was entitled to assume any period as fundamental and I did not therefore regard the ordinary processes of harmonic analysis as applicable to this particular case.*

But at the time when my evaluation of the six components was completed I had the advantage of the assistance of Mr. H. E. Wood, Chief Assistant in the Transvaal Meteorological Service, who was working in the Meteorological Office for a period preparatory to his taking up his appointment in South Africa, and he was good enough to undertake the treatment of the figures for the yield of wheat on more orthodox methods.

He analysed harmonically the 11 years' period from 1891 to 1902 with the following results:—

Mean value ...	30·47 bushels.						
Period.....	11	$\frac{11}{2}$	$\frac{11}{3}$	$\frac{11}{4}$	$\frac{11}{5}$	$\frac{11}{6}$	years.
Amplitude	2·74	0·76	2·68	2·54	2·04	2·04	bushels.
Node (nearest year)	1896 (+)	1895 (+)	1896 (−)	1896 (+)	1895-6 (+)	1895-6 (+)	

\+ means ascending, − descending.

It will be seen that except for the amplitudes of the fifth and sixth components the result is not very different from that which I obtained by a less regular process from a study of the values for the whole twenty years.

When the calculation derived from the analysis is extended to give

* The advantage of supposing that the components do not belong to a harmonic series is that any group of non-harmonic components, if persistent, must ultimately concur in a node, but the node and consequent reversal need not recur until after the lapse of what Professor Chrystal calls a "configuration period," which may be very long.

values for comparison with the whole series of 21 years, the errors are somewhat greater and the two-year oscillation is too conspicuous in the calculated values. The amplitude depends upon a single number in the harmonic computation and is therefore not capable of very accurate evaluation. The calculated value for 1905 is 32·8 bushels and is therefore a little further from actuality than the figure derived from my computation.

Mr. Wood also calculated the periodogram for the observations according to the method indicated by Professor Schuster. The periods dealt with were of 2, 3, 4 . . . up to 14 years and thereafter 16 years and 18 years. The method is from the nature of the case not very effective with data of such limited extent. Moreover, as there is only one wheat value for a whole year the components of 11 years cannot be well represented. Still the periodogram shows a prominence for a variation of an 11 years' period; 11/2 is less marked, 11/3 is very prominent, 11/4 is just indicated.

One point in connection with the periodogram affords, as I understand it, a strong confirmation of the views represented in this paper. The ordinate representing the amplitude for the period of two years is *zero*. This result surprised me at first because the fluctuations from year to year are a most conspicuous feature of the line representing the actual values. My estimate of the amplitude of the fifth and sixth components which combine to give an oscillation of two years' period is 1 bushel; Mr. Wood's value, calculated from the data for 1891 to 1902, is 2 bushels. But the disappearance of the two-year oscillation from the periodogram deduced from 20 years' values is easily explained if the fluctuation is really the result of the "beat" of two components, one slightly greater and the other slightly less than two years. If the two components are equal in amplitude, the fluctuation, which is the combination of the two, changes its phase to the opposite in five and a-half years, so that the average fluctuation taken over 11 years should show no two-year oscillation at all; similarly, on the average of 22 years there should be no two-year oscillation, and the combination of the figures for 20 years, to give the periodogram ordinate for the two-year oscillation, shows that this inference is borne out by the actual numbers.

The periodogram, therefore, confirms the result that the two-year oscillation which is very conspicuous at some parts of the cycle is really a combination of two oscillations of nearly equal period which alters its phase within 20 years in such a way that on the average of the whole period there is no oscillation of two years' period at all, in other words, the even years are on the average neither better nor worse than the odd years.

The singular agreement between the actual figures and those derived from the periodic values for 11 years with its harmonic components may be attributed to chance by those who desire to adopt that explanation. It is certainly difficult to see how wheat can have much to do with variations which are periodic in a fraction of a year, even though the fraction be an improper one. But here again a curious point is disclosed. Those terms are most accentuated of which the periods come nearest to an exact number of years; the amplitudes and periods are (taking my own estimates):—

Amplitudes.....	2·9	0·5	1·8	2·8	1·0	1·0.
Periods	11	5·5	3·67	2·75	2·2	1·83.

The least conspicuous component is that of five and a-half years, which has its maximum alternately in summer and winter, or other opposite periods of the year. The fourth component is stronger than the third; it is more nearly periodic in an exact number of years.

The fifth and sixth components together when they are in concurrence give a result greater than that of the third, and the period of the combined effect is of two years.

Thus there are subsidiary points which seem to discredit to a certain extent the doctrine of chance as an explanation of the fact from which the investigation started, namely, that the excesses and defects of the yield balance one another about the years 1895—6. Nor can I myself regard it as a matter of chance that a law of sequence derived from observations of a number of years continues to hold for extrapolations both in the past and in the future. I cannot see any other conclusion consonant with the facts but this—that during the 21 years—1885 to 1905—the yield of wheat in Eastern England has been very nearly identical with the sequence given by a periodic variation of 11 years and its five harmonic components. When one considers the vicissitudes to which the wheat crop is exposed, before the yield is estimated for the Board of Agriculture, it must be regarded as very remarkable not that there are exceptions to the law of sequence, but that there are so few of any importance.

Whether the law of sequence will continue to be that indicated by the composition of the curve for 21 years is another matter. The fundamental period may not be exactly 11 years; the components may prove to be after all not exactly the harmonics of the 11-year fundamental. Presumably we must wait until additional data have accumulated. It does not follow that the law, if true for the particular district I have chosen, the "England East" of the Meteorological Office, is necessarily true for every

county or every field. The data for two years taken at random indicate that the counties are differently affected in different years:—

Year.	Bedford.	Cambridge.	Essex.	Hertford.	Huntingdon.	Norfolk.	Suffolk.	England, East.
1903.....	29·5	31·4	28·8	28·2	30·5	33·1	29·4	30·4
1902.....	32·1	33·1	34·4	31·9	33·1	34·3	32·9	33·4

On that account I have not attempted to trace the relationship in the data compiled for different localities for longer periods.

A variation of about 11 years' period has been suggested for various solar and terrestrial phenomena, but I know of no case in which the sequence of phenomena is so completely accounted for in magnitude and direction as in the case of the yield of wheat for Eastern England. If it is not a matter of chance, and that seems too improbable, it must be a matter of considerable importance.

Table: Yield of Wheat for Eastern England.

1	2	3	4	5	6	7
Year.	Previous autumn rainfall in inches.	Yield computed from previous autumn rainfall (p. 70).	*Actual yield* in bushels per acre.	Yield computed from six harmonic components (p. 71).	Yield computed from the analysis of the yields 1891–1902 (Mr. Wood, p. 72).	Difference between calculated (column 5) and actual yield (column 4).
1885	7·30	29·9	33·8	35·3	36·2	+1·5
1886	12·63	18·2	29·2	30·1	26·6	+0·9
1887	6·92	30·8	32·9	35·6	37·7	+2·7
1888	6·67	31·3	31·9	35·5	37·6	+3·6
1889	5·37	34·2	29·3	28·8	28·1	−0·5
1890	6·90	30·8	31·8	31·0	31·7	−0·8
1891	5·60	33·7	33·5	33·2	32·9	−0·3
1892	8·22	27·9	26·0	26·5	26·9	+0·5
1893	10·19	23·6	25·2	26·4	23·7	+1·2
1894	6·86	30·9	31·1	31·9	32·8	+0·8
1895	7·90	28·6	27·7	26·7	25·6	−1·0
1896	6·74	31·2	34·4	35·3	36·2	+0·9
1897	9·49	25·1	28·5	30·1	26·6	+1·6
1898	5·14	34·7	36·3	35·6	37·7	−0·7
1899	5·23	35·1	34·2	35·5	37·6	+1·3
1900	7·83	28·8	27·5	28·8	28·1	+1·3
1901	4·83	35·4	31·8	31·0	31·7	−0·8
1902	4·78	35·5	33·4	33·2	32·9	−0·2
1903	4·26	36·6	30·4	26·5	26·9	−3·9
1904	8·96	26·3	25·2	26·4	23·7	+1·2
1905	3·80	37·6	32·0	31·9	32·8	−0·1

This study arose out of the consideration of the relation between the autumn rainfall and the yield of wheat of the subsequent year. The relation as concerning the yield of wheat for Great Britain was the subject of a preliminary note to the Royal Society in February, 1905. The corresponding relation for the East of England is—

$$W = 46 - 2{\cdot}2\ R,$$

where W is the yield in bushels per acre and R the rainfall of the previous autumn. The figures from which this relation is computed are given in the table on the previous page, and a column of values derived from the formula is also given.

It is clear that the rainfall is subject to no such rigorous law of sequence as the wheat crop. A relation between the autumn rainfall and the wheat crop is sufficiently manifest, but evidently the fall of rain is subject to disturbances of an irregular character which have little counterpart in the curve of wheat values.

The Electrostatic Deviation of α-Rays from Radio-Tellurium.

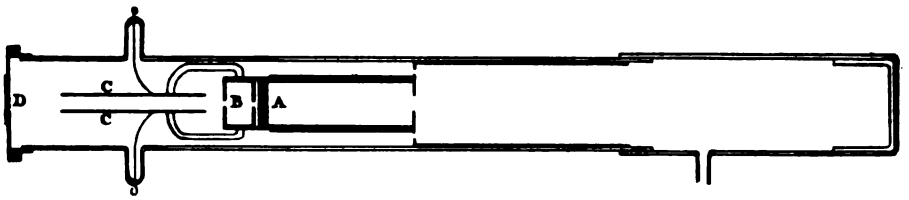
By W. B. Huff, Associate Professor of Physics, Bryn Mawr College, Pa., U.S.A.

(Communicated by Professor J. J. Thomson, F.R.S. Received June 27,— Read June 28, 1906.)

A determination of the electrostatic deviation of the α-rays from radio-tellurium was suggested to the writer by Professor J. J. Thomson, as a continuation of the work on α-rays done by Professor A. S. Mackenzie.*

The general plan of the work was to let a beam of the rays pass between two charged plates, and then fall upon a glass plate coated with a thin layer of zinc sulphide on the side receiving the radiation. A photographic plate in contact with the other side of this fluorescent screen would be affected by the scintillations and thus mark the position of the beam.

The arrangement of the apparatus used is shown by the diagram. The radiation from the disc at A, passing through the brass slit-tube B, and between the charged plates C, reaches the fluorescent screen D.



A copper disc, coated with radio-tellurium by Sthamer, served as the source of the rays. The slits were 0·2 mm. and 8 mm. apart. Over the outer slit was a sliding magnet (not shown on the diagram), which made it possible to shield the screen from the rays when no field was on. Quartz rods supported the condenser plates, which were of thin steel, 4 cm. long and 1·4 cm. wide. The ends of these plates were 0·6 cm. and 1·5 cm. from the slit-tube and fluorescent screen respectively.

These parts of the apparatus were supported by a long split-ring, which fitted closely in a glass tube 3·3 cm. in diameter. This tube was vertical, the lower end being waxed into a larger tube which contained phosphorous pentoxide, and connected with the mercury pump. The wires from the

* 'Phil. Mag.,' vol. 10, 1905.

Wimshurst machine were soldered to the steel condenser plates, and sealed into glass side tubes. The fluorescent screen was 2 cm. square and 0·35 mm. thick. The coated area was 5 mm. square. This plate was waxed to a brass cap, the latter being waxed to the upper end of the large glass tube, which contained the condenser plates, slit-tube, etc.

The vacuum was as good as could be got with a mercury pump. After the tube was exhausted, the scintillations could be seen with a lens, but they were too few to make eye-measurements possible. Even when using the most sensitive photographic plates, exposures of 40 or 50 hours gave lines which were extremely hazy. Scintillations, and therefore photographs, can be obtained when the rays traverse considerably greater distances than those indicated in the figure; but with narrow slits the time required is very long; with wide slits, the lines are too broad to be of use.

When the rays are allowed to fall directly upon the photographic plate, an impression, of about the same density as that got with a screen, is considerably wider. This effect, due to a screen, suggested using a very thin one over the photographic plate, the combination being sealed into the vacuum tube. A screen $\frac{0·1}{\cdot\cdot}$ mm. thick was tried in this way. When no field was on a good plate was obtained, but with the field on the plate invariably fogged, even when the tube was allowed to stand for several days after being pumped out, and when the electrometer had given no evidence that sparking had occurred. Plates showing the double deviation were obtained, but fog rendered them worthless.

It was finally decided to fasten a metal frame to the outside of the brass cap over the upper end of the tube, and to fit photographic plates accurately into this. By choosing plates with smooth edges it thus became possible to measure the distance of a single line from the edge of the photographic plate parallel to it. By using wider slits denser lines were got, and this, it seemed probable, would more than compensate for the errors introduced by having to compare separate plates.

Using this method, several plates have been obtained. Exposures of 60 hours each gave three fairly clear lines. Using these plates, the following measurements were taken for the double deviations.

mm.	mm.
1·20	1·25
1·52	1·35
1·20	1·40

$$2d = 1·32 \text{ mm.},$$

or 0·66 mm. for the deviation one way.

The variations in the separate measurements indicate the difficulty in setting on lines which are, at best, extremely hazy.

Calculating $\int dx \int \mathrm{F}\, dx$,*

and using the relation $\frac{mv^2}{e} = \frac{10^8}{d} \int dx \int \mathrm{F}\, dx$,†

we obtain $\frac{mv^2}{e} = 4{\cdot}64 \times 10^{14}$.

Since $\frac{mv}{e} = 3{\cdot}30 \times 10^5$,‡

we derive the values—

$$v = 1{\cdot}41 \times 10^9,$$

$$e/m = 4{\cdot}3 \times 10^3 \text{ in electro-magnetic units.}$$

This result is considerably less than the corresponding quantity for radium. The chief source of possible error lies in the difficulty of making accurate settings on a broad hazy line.

I desire to record my thanks to Professor J. J. Thomson for extending to me the privileges of the Cavendish Laboratory, and for advice and suggestions always generously given.

* Maxwell, 'Electricity,' § 202.

† J. J. Thomson, 'Conduction of Electricity through Gases,' § 50.

‡ Mackenzie, *loc. cit.*

An Investigation of the Influence of Electric Fields on Spectral Lines: Preliminary Note.

By Professor G. F. HULL, Dartmouth College, U.S.A.

(Communicated by Professor J. Larmor, Sec. R.S. Received and read June 28, 1906.)

In general the electrical fields used were those concomitant with the luminous electric discharge. An interferometer of the Michelson form and an echelon spectroscope of 18 plates were used to analyse the radiations. The results may be summarised as follows:—

(1) End-on discharge tubes of special design, in which the light-source was a uniform column of luminous mercury vapour viewed in the direction of discharge, showed no change of wave-length as great as 1 part in 4,000,000 when the direction of the discharge was reversed. The pressure in the tube was varied from a few millimetres to a vacuum so high that there was but little luminosity.

(2) The passage of Röntgen rays through the tube did not alter the wave-length nor the width of the mercury lines, to an extent sufficient to affect the visibility of interference fringes formed with a difference of path of 400,000 waves. When the luminous column was viewed at right angles to the direction of the discharge no polarisation effects in the radiation from it, due to the passage of the Röntgen rays, could be detected by a sensitive Savart plate and Nicol prism.

(3) When the discharge passed in air between electrodes formed of an amalgam of cadmium and mercury, no variation of the wave-lengths of the strong Cd, Hg, lines greater than 0·002 tenth-metres was obtained, by changing the line of sight from a direction along the discharge to one at right angles to that direction. Approximately the same result held good when a small capacity was inserted in the circuit, but in this case the discrepancies in the readings were larger.

This result shows that the luminous particles do not acquire a velocity in the direction of the discharge greater than 150 metres per second. Hence the curving of the image of the discharge produced by a rotating mirror, as in the Feddersen experiment, and as recently studied by Schuster and Hemsalech for individual spectral lines, appears to be due not so much to motion of luminous particles as to the propagation along those particles of a condition of luminosity.

(4) Doppler effects in the canal rays, as announced by Stark during the course of the present investigations, were found for the strong hydrogen

lines. In some cases they appeared also in mercury lines. The velocities represented by the displacements of the lines were of the order of 4×10^5 metres per second for the hydrogen particles and $2{\cdot}5 \times 10^4$ metres per second for those of mercury. But it was found that, in general, the luminous mercury particles in the canal rays did not move, at any rate with a velocity greater than 100 metres per second. In these cases the canal rays appear to be due to non-luminous particles streaming through the mercury vapour and producing luminescence in the latter, probably by bombardment.

(5) A glass tube was sealed on to a canal-ray tube, at right angles to the direction of the rays. This tube was covered by a piece of optical glass as free as possible from strain. A very sensitive combination of Savart plate and Nicol prism was used to detect, if possible, any polarisation that might exist in the light from the rays in hydrogen. After eliminating reflections from the walls of the tube no polarisation could be recognised.

(6) The light produced by electrical discharge, in uniform tubes 3 or 4 cm. in diameter, was examined perpendicular to the direction of discharge, at various points between the electrodes and also behind the perforated cathode. It was found that the principal hydrogen lines were greatly broadened in those parts where the electric field is known to be of great intensity. For example, the luminous layer covering the cathode (the dark space being 0·5 to 4 cm.) gave hydrogen lines 0·4 Angström units in width, but the lines of the second hydrogen spectrum and certain air lines were not appreciably broadened. This broadening seems to be due mainly to motion of the particles rather than change of free periods, for it is found to the same extent behind the cathode in the canal rays. The broadening is so great that it is not possible with the instruments at the writer's disposal to determine the shift of these lines except to fix a superior limit of 0·1 A.U. to its possible magnitude. The amount is probably considerably less than this. On the other hand, the shift of the lines of the second spectrum of hydrogen is so small as to approach the limits of error, viz., 0·005 A.U. The mercury lines show no shift but a slight broadening.

The experiments thus show that any electrical analogue of the Zeeman effect is, under the above conditions, largely masked by a widening of the lines.

The work was carried out at the Cavendish Laboratory, Cambridge, during the past winter; and the writer's thanks are due to Professor J. J. Thomson and to Professor Liveing for the facilities kindly accorded to him.

The Affinity Constants of Amphoteric Electrolytes. I.—*Methyl Derivatives of Para-aminobenzoic Acid and of Glycine.*

By JOHN JOHNSTON, B.Sc., A.I.C. (Carnegie Research Scholar).

(Communicated by Professor James Walker, F.R.S. Received May 21,—Read May 31, 1906.)

(From the Chemical Laboratory, University College, Dundee.)

The following investigation was undertaken in order to determine the influence on the basic and acidic constants of successive introductions of a methyl group into an amino-acid, including the effect of changing the acid into the corresponding methyl ester. Two series of compounds were investigated, namely, the methyl derivatives of *p*-aminobenzoic acid and of glycine. Constants for *p*-aminobenzoic acid, glycine, and some of its methyl derivatives had already been determined by Winkelblech.*

Methods.

Whenever practicable the basic constant k_b was determined by means of the catalysis of methyl acetate, using the comparison method of Walker and Wood.† The end point was determined in a separate experiment with decinormal hydrochloric acid; and it was found that the same result was obtained whether or not the bottle containing the reaction mixture had been opened to admit of intermediate readings being taken. In every case 1 c.c. at a time was withdrawn and titrated with N/20 caustic soda, which had been prepared from sodium and conductivity water; and unless otherwise stated, phenolphthalein was used as indicator.

In the tables v refers to the dilution of the solution after mixture, A is the total range of the reaction, and c is the constant for a monomolecular reaction.

In cases where the catalysis method was inapplicable, recourse was had to the Löwenherz solubility method, which was carried out as follows: A flask containing a known weight of substance mixed with a known volume of standard hydrochloric acid was kept in the thermostat for at least a day, being shaken from time to time. The liquid was then filtered through a tared paper, and the paper and contents—the amount left undissolved—were dried until of constant weight. The solubility in water was determined by a similar method.‡

* 'Zeit. für physikal. Chem.,' vol. 36, p. 546, 1901.

† 'Journ. Chem. Soc.,' vol. 83, p. 484, 1903.

‡ Compare Wood, 'Journ. Chem. Soc.,' vol. 83, p. 572, 1903.

In one case, owing to the impracticability of either of the above methods, the basic constant was determined by the distribution method of Farmer and Warth.* Known weights of substance were shaken up with known volumes of benzene and water, and of benzene and standard hydrochloric acid. The amount of free base present in the benzene layer was determined by experiment, allowance being made for the mutual solubility of benzene and water; the amount of base in the aqueous layer was obtained by difference. From the data obtained in this way, the basic constant, k_b, was calculated.

The acidic constant k_a was determined by means of conductivity measurements or by the salt-hydrolysis method of Shields.†

The conductivity measurements were effected in the usual way, but it was found that in most cases unplatinised electrodes gave better results than platinised electrodes, owing, apparently, to a certain amount of absorption of the substance by the latter. The water used had a conductivity not greater than $1{\cdot}5 \times 10^{-6}$ at 25°; no correction was made for the conductivity of the water. From the measurements the acidic constant was calculated by means of the equations established by Walker.‡ The symbols used have the same significations as in those papers.

The solution for the hydrolysis method of Shields was prepared as follows. To a measured volume of a standard solution of pure soda was added the equivalent quantity of the substance. When this solution had reached the temperature of the thermostat, the equivalent amount of a solution of methyl acetate—also at 25°—was added. After shaking, 5 c.c. of the mixture was immediately withdrawn and titrated with 0·0252 N hydrochloric acid, using nitrophenol as indicator. When the reaction proceeded very rapidly, this initial titre was obtained by calculation. At suitable intervals, other portions of 5 c.c. were withdrawn and titrated similarly.§

As equivalent concentrations of salt and methyl acetate were employed, the calculation is somewhat simpler than that given by Shields. If E is the original concentration of methyl acetate and of the salt, x the amount transformed in time t, c the constant regulating the equilibrium between the hydrolysed and unhydrolysed portions of the salt, and k the saponification constant for caustic soda, then

$$kc\,dt = \frac{x\,dx}{(E-x)^2},$$

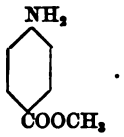
* 'Journ. Chem. Soc.,' vol. 85, p. 1713, 1904.
† 'Zeit. physikal. Chem.,' vol. 12, p. 167, 1893.
‡ 'Roy. Soc. Proc.,' vol. 73, p. 155, vol. 74, p. 271, 1904.
§ *Cf.* Shields, *loc. cit.*

which on integration between the proper limits gives

$$c = \frac{1}{kt}\left[\frac{E}{E-x} - 1 - 2{\cdot}303 \log_{10} \frac{E}{E-x}\right].$$

The value of k_a is obtained from the equation $k_a = K/c$, in which K is the dissociation constant of water, and is equal to $1{\cdot}21 \times 10^{-14}$ at 25°. The use of the above formula is inadmissible when the degree of hydrolysis is great. This is the case with the betaines investigated. These were compared directly with a similar solution of pure caustic soda; and the rates of reaction in the two cases proved to be almost identical.

The experiments throughout the investigation were carried out at a temperature of 25°.

Methyl Ester of p-Aminobenzoic Acid, 

A solution of the acid in absolute methyl alcohol was saturated with hydrochloric acid gas, and boiled under a reflux condenser for five hours. On cooling, crystals of the ester hydrochloride separated, which, on recrystallisation from methyl alcohol, yielded plates of a slightly yellowish colour.

Chlorine found..... ... I, 19·0; II, 18·86 per cent.
$C_6H_4(COOCH_3)NH_2HCl$ requires Cl..... 18·93 „

The amount of halogen was in this and in all similar cases determined by Volhard's method.

On neutralising a solution of the hydrochloride with ammonia, the ester was precipitated, and was recrystallised from methyl alcohol as white plates melting at 112°.*

Comparison Solutions.

N/15 Cl solution (20 per cent. HCl, 80 per cent. KCl) $c = 0{\cdot}0000380$
„ „ (30 „ 70 „ „) $c = 0{\cdot}0000570$

Hydrolysis in I $= 20 \times \frac{457}{380}$; in II $= 30 \times \frac{452}{570}$.
$= 24{\cdot}05$ per cent. $= 23{\cdot}8$ per cent.

Now if x is the hydrolysed proportion, v the dilution, and K the dissociation constant for water,

$$\frac{k_b}{K} = \frac{(1-x)v}{x^2}.$$

* Compare Einhorn, 'Liebig's Annalen,' vol. 311, p. 158, 1900.

Hence

$$\text{I.}\quad \frac{k_b}{K} = \frac{0{\cdot}76 \times 15}{(0{\cdot}24)^2}; \qquad \text{II.}\quad \frac{k_b}{K} = \frac{0{\cdot}762 \times 15}{(0{\cdot}238)^2}.$$

$$= 198. \qquad = 202.$$

Mean value for $k_b/K = 200$.

Determination of Basic Constant—Catalysis Method.

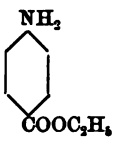
0·1875 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 15$, $A = 15{\cdot}40$.

I.

t.	Titre.	*x.*	A−*x.*	*c.*
0	1·27	0	15·40	—
2265	4·50	3·23	12·17	0·0000452
2474	4·80	3·53	11·87	457
2866	5·31	4·04	11·36	461
3725	6·23	4·96	10·44	453
4021	6·59	5·32	10·08	458
4348	6·90	5·63	9·77	454
5158	7·74	6·47	8·93	458
5452	7·98	6·71	8·69	456
5741	8·30	7·03	8·37	461
6581	9·00	7·73	7·67	460
			Mean	0·0000457

II.

t.	Titre.	*x.*	A−*x.*	*c.*
0	1·22	0	15·40	—
1506	3·46	2·24	13·16	0·0000454
2621	4·88	3·66	11·74	449
2957	5·30	4·08	11·32	452
4016	6·48	5·26	10·14	452
4450	6·90	5·68	9·72	449
5430	7·89	6·67	8·73	454
			Mean	0·0000452

Ethyl Ester of p-Aminobenzoic Acid, 

This substance was prepared by a method analogous to that adopted for the methyl ester. The hydrochloride, when recrystallised from methyl

alcohol, separated in shining white plates, which melted at 206° to 207° with decomposition.

Chlorine found..... 17·48 per cent.
$C_6H_4(COOC_2H_5)NH_2HCl$ requires Cl..... 17·62 „

The ester was liberated by treatment of the hydrochloride with ammonia. It recrystallised from aqueous alcohol in the form of fine white needles melting at 91°.

Determination of Basic Constant—Catalysis Method.

0·2015 gramme hydrochloride in 20 c.c. water, 1 c.c. MeAc, $v = 20$, $A = 12·07$.

I.

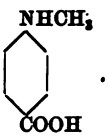
t.	Titre.	x.	$A-x$.	c.
0	0·98	0	12·07	—
2,422	3·20	2·22	9·85	0·0000364
5,337	5·30	4·32	7·75	360
5,682	5·57	4·59	7·48	366
6,742	6·20	5·22	6·85	365
7,267	6·46	5·48	6·59	362
8,189	6·97	5·99	6·08	364
8,755	7·29	6·31	5·74	369
9,644	7·70	6·72	5·35	366
10,002	7·85	6·87	5·20	366
			Mean	0·0000365

II.

t.	Titre.	x.	$A-x$.	c.
0	0·98	0	12·07	—
2744	3·43	2·45	9·62	0·0000359
3088	3·75	2·77	9·30	366
4148	4·50	3·52	8·55	360
4674	4·86	3·88	8·19	360
5596	5·46	4·48	7·59	360
6162	5·83	4·85	7·22	362
7051	6·35	5·37	6·70	362
7409	6·55	5·57	6·50	363
			Mean	0·0000361

Comparison Solutions.

N/20 Cl solution (25 per cent. HCl, 75 per cent. KCl), $c = 0·0000361$.
„ „ (20 „ 80 „), $c = 0·0000290$.
Hence k_b/K = I, 236; II, 240.
Mean value of $k_b/K = 238$.

p-Methylaminobenzoic Acid, 

.

Twenty-five grammes of *p*-aminobenzoic acid were dissolved in the equivalent quantity of an aqueous solution of caustic soda of about 8 per cent. strength. To the cooled solution, one equivalent of methyl sulphate was added, and the mixture was kept cool, and shaken from time to time. After one and a half hours the reaction was practically complete, the mixture having become quite pasty. The solid was filtered off on the pump, dried and recrystallised from boiling water. The yield of crude substance was almost quantitative. When recrystallised, it consisted of small white needles, which on drying turned slightly yellow, melting at 144° to 145°; and this melting point remained unchanged after recrystallising twice from water, alcohol, or benzene.

0·2028 gramme substance gave 0·4716 gramme CO_2 and 0·1076 gramme H_2O.

I. 0·2645 gave 20·3 c.c. moist N, measured at 16° and 764 mm.
II. 0·2420 „ 18·6 „ „ „ 15 „ 773 „

	C. per cent.	H. per cent.	N. per cent.
Found	63·42	5·90	I, 9·0 II, 9·15
$C_6H_4(NHCH_3)(COOH)$ requires	63·57	5·96	9·29

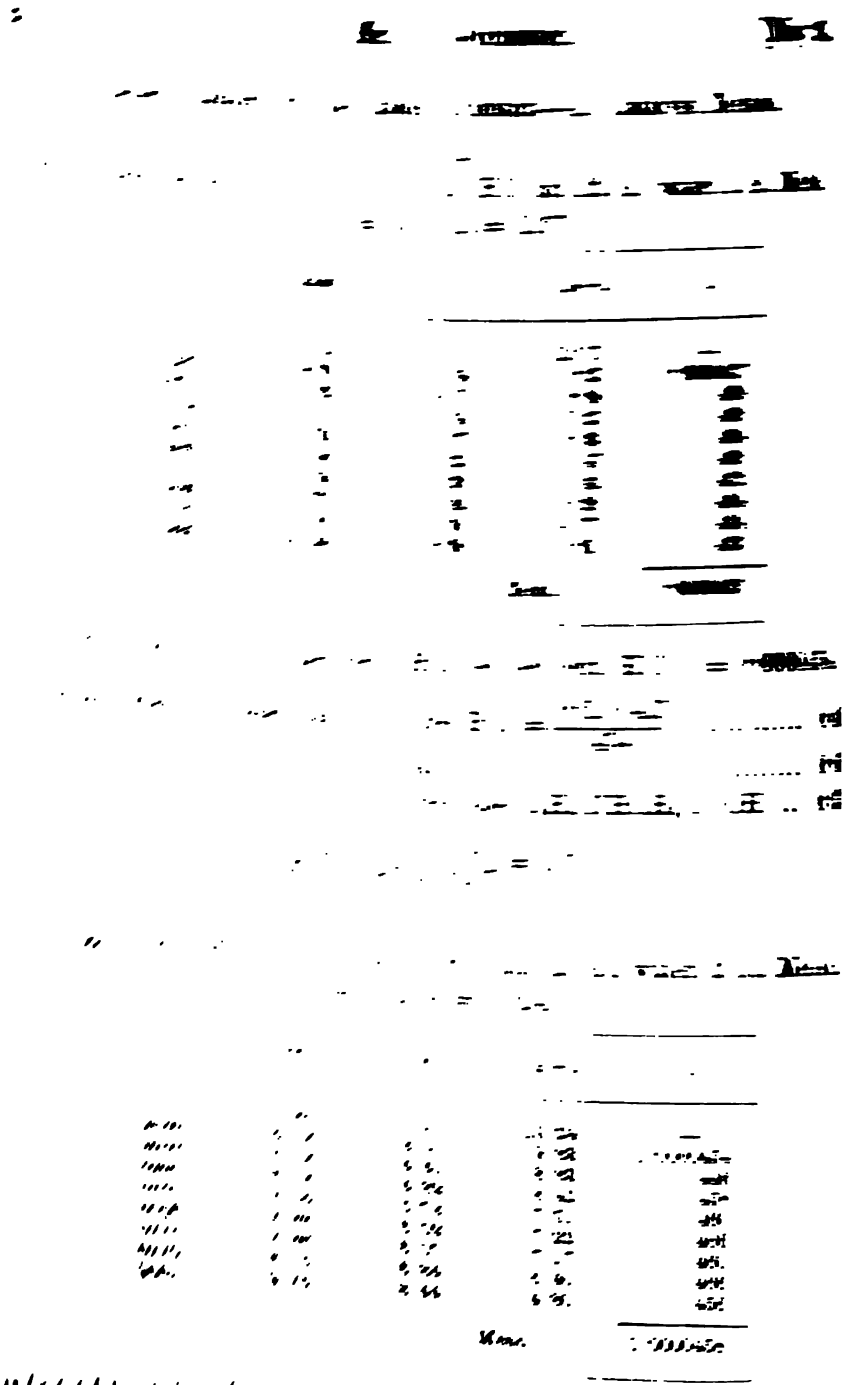
As the direct determination of nitrogen in the case of the aminobenzoic acids tends to give low results, the percentage of nitrogen was redetermined by Kjeldahl's method.

0·4605 gramme gave ammonia equivalent to 0·0431 gramme N = 9·37 per cent.

The same product was also obtained by the action of methyl iodide on *p*-aminobenzoic acid, but the yield was much smaller, and the isolation and purification of the acid were more troublesome.

p-Methylaminobenzoic acid has an acid reaction to ordinary indicators, and can be roughly titrated by means of *o*-nitrophenol, which changes colour when about 94 per cent. of the acid present has been neutralised.

It is soluble in alcohol and benzene, though not very soluble in cold water, and is to a slight extent volatile in steam. The alkali salts are freely soluble in water; and from their aqueous solutions the free acid can be recovered by the cautious addition of hydrochloric acid, excess of which must be avoided, since it redissolves the acid with formation of the hydrochloride.



B. Löwenherz Solubility Method.

Amount dissolved by 1000 c.c. water	1·79 grammes.
Whence concentration of base in water (solubility)	0·0119 N.
Amount dissolved by 50 c.c. 0·1022-N HCl.....	0·549 gramme.
Whence total concentration of base $C_6H_4(NHCH_3)COOH$	0·0727 N.
Therefore concentration of salt	0·0608 N.
And concentration of free HCl	0·0414 N.

$$\frac{k_b}{K} = \frac{0{\cdot}0608}{0{\cdot}0119 \times 0{\cdot}0414} = 124.$$

General mean of $k_b/K = 137$.

Determination of the Acidic Constant k_a—Conductivity Method.

Conductivity of the Sodium Salt.—As the salt does not crystallise well, the solutions were made up by adding the calculated quantity of acid to a standard solution of soda, made from sodium and CO_2-free water.

v	32	64	128	256	512	1024
μ, I	68·2	71·6	72·9	75·3	77·3	80·5
II	68·5	71·7	72·7	75·5	77·6	81·0

The figures under I and II were obtained from distinct solutions: from the above $\mu_{1024} - \mu_{32} = 12{\cdot}4$, which is about the normal value for non-hydrolysed sodium salts.

The speeds of the hydrogen and sodium ions are 347 and 51 respectively: so that

$$\mu_\infty \, H^+, XOH^- = 81 + 347 - 51 = 377,$$

and

$$\mu_\infty \, HX^+, XOH^- = (81 - 51) + (81 - 51 + 6) = 66.$$

For the method of obtaining the value of $\mu_\infty \, HX^+, XOH^-$, compare Walker.*

Conductivity of the Acid.—Sample I was recrystallised from water, sample II from benzene. The solution at each dilution was made up separately, as the use of pipettes is not advisable when dealing with solutions of such feeble conducting power.

v.	μ.		m.	$k_0 \times 10^5$.
	I.	II.		
128	10·2	10·2	0·0271	0·59
256	15·6	15·6	0·0415	0·70
512	23·7	23·6	0·0629	0·82
1024	34·1	34·2	0·0908	0·88

* *Loc. cit.*

It is evident that the Ostwald "dissociation constant" k_0 has here no real application, since it rises by 50 per cent. in the comparatively small range of dilutions studied.

Conductivities calculated from Walker's equations.

$k_a = 0{\cdot}92 \times 10^{-5}$, $k_b/K = 137$, μ_∞ $H^+, XOH^- = 377$, μ_∞ $HX^+, XOH^- = 66$.

v.	a.	d.	μ.	m.	$k_0 \times 10^5$.
128	$18{\cdot}3 \times 10^{-5}$	$18{\cdot}2 \times 10^{-5}$	10·3	0·0275	0·61
256	14·9	7·4	15·6	0·0415	0·70
512	11·5	2·8	23·1	0·0614	0·79
1024	8·5	1·0	33·5	0·0891	0·85

The divergence between the experimental and the calculated values of μ does not exceed the conductivity of the solvent water.

Methyl Ester of p-Methylaminobenzoic Acid,

was prepared by an analogous method to that given on p. 84. In this case, however, the hydrochloride did not separate out, and the ester was precipitated by means of sodium carbonate. It crystallised from ligroin in the form of small white plates, melting at 75° to 76°.

	per cent.
0·1860 gramme gave ammonia equivalent to 0·0155 gramme N ...	8·35
$C_6H_4(NHCH_3)(COOCH_3)$ requires N	8·48

This substance is soluble in benzene, alcohol, and ether, although it does not crystallise well from them, but it is almost insoluble in water.

Determination of Basic Constant—Distribution Method.

	Amount of benzene layer.	Amount of aqueous layer.	Total base taken.	Base in benzene layer.	Base in aqueous layer.	Distribution ratio = F.
	Distribution between benzene and water.					
	c.c.	c.c.	gramme.	gramme.	gramme.	
	14·7	500	0·1308	0·1073	0·0235	157
	14·7	490	0·1815	0·1505	0·0310	163
	Distribution between benzene and 0·1022 N HCl.					
	c.c.	c.c.	gramme.	gramme.	gramme.	
I	10	95	0·3005	0·146	0·1545	—
II	10	95	0·2500	0·126	0·124	—

From I—

Concentration of free base in water $= \frac{0{\cdot}0146}{160 \times 0{\cdot}165}$ ..... 0·00055 N.

Concentration of total base..... 0·00986 N.

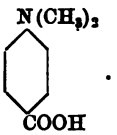
Whence concentration of salt is 0·00932 N, and of acid ... 0·0929 N.

Therefore $\frac{k_b}{K} = \frac{0{\cdot}00932}{0{\cdot}0929 \times 0{\cdot}00055}$..... 182.

Similarly, from II—

$\frac{k_b}{K} = \frac{0{\cdot}00744}{0{\cdot}0948 \times 0{\cdot}000476}$ ..... 164.

Mean value of $k_b/K = 173$.

p-Dimethylaminobenzoic Acid, 

.

By the action of methyl sulphate upon the crude *p*-methylaminobenzoic acid the process of methylation can be carried one step further. The mode of procedure is identical with that described for the preparation of the monomethyl acid. By recrystallising the product from 50 per cent. aqueous alcohol, *p*-dimethylaminobenzoic acid separates out in fine white needles, which melt at 235° to 236°, and are identical with the product obtained by the action of phosgene on dimethylaniline.* The yield is practically quantitative.

p-Dimethylaminobenzoic acid, though soluble in alcohol, is not very soluble in ether or benzene, and is almost insoluble in water.

Determination of Basic Constant—Solubility Method.

Solubility in Water.

A. Solution superheated— I, 0·074, II, 0·072 gramme per litre
B. „ not superheated—I, 0·074, II, 0·072 „ „
= 0·00044 N.

I. Solubility in 0·100 N HCl = 0·00182 gramme per c.c. = 0·01103 N.
II. „ 0·1022 N HCl = 0·00186 „ „ = 0·01127 N.

From I— $\frac{k_b}{K} = \frac{0{\cdot}01059}{0{\cdot}08941 \times 0{\cdot}00044} = 269.$

And from II— $\frac{k_b}{K} = \frac{0{\cdot}01083}{0{\cdot}09137 \times 0{\cdot}00044} = 269.$

Mean value of $k_b/K = 269$.

* Michler, 'Berichte,' vol. 9, p. 401, 1876.

Determination of the Acidic Constant.—The only practicable way of effecting this was by conductivity measurements, and this could only be done at one dilution. The Shields method was tried, but the insolubility of the acid prevented accurate titration, and rendered the method invalid.

Conductivity of the Sodium Salt.

v	32	64	128	256	512	1024
μ	67·0	69·7	72·4	74·7	77·1	79·0

The difference, $\mu_{1024} - \mu_{32} = 12$, is again nearly normal, showing that there is not much hydrolysis.

Calculating as on p. 89,

$$\mu_\infty \, H^+, XOH^- = 375,$$
$$\text{and} \quad \mu_\infty \, HX^+, XOH^- = 62.$$

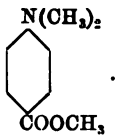
Conductivity of the Acid.

	μ.				
v.	I.	II.	III.	m.	k_0.
2260	49·0	49·0	49·0	0·1302	$0{\cdot}86 \times 10^{-5}$

I, II, and III were distinct solutions.

Conductivity calculated from $k_a = 0{\cdot}94 \times 10^{-5}$, $k_b/K = 269$, and from the above values for μ_∞.

v.	a.	d.	μ.	m.	k_0.
2260	$56{\cdot}6 \times 10^{-6}$	$5{\cdot}6 \times 10^{-6}$	48·9	0·1300	$0{\cdot}86 \times 10^{-5}$

Methyl Ester of p-Dimethylaminobenzoic Acid, 

This ester was prepared in the same way as the ester of the monomethyl acid; it recrystallises from ethyl alcohol in white plates, melting at 102°.*

Determination of the Basic Constant.—The distribution method was tried, but proved unsatisfactory, owing to the excessive magnitude of the distribution-ratio between benzene and water. The constant was determined by the solubility method.

* *Cf.* Bischoff, 'Berichte,' vol. 22, p. 343, 1889.

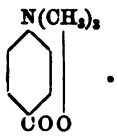
	Solubility in water	= 0·160 gramme per litre	.....	0·00089 N.
I.	„ 0·0252 N HCl	= 1·05 „ „	.....	0·00587 N.
II.	„ 0·1022 N HCl	= 3·76 „ „	.....	0·0210 N.

From I— $\frac{k_b}{K} = \frac{0{\cdot}00498}{0{\cdot}0202 \times 0{\cdot}00089} = 277.$

And from II— $\frac{k_b}{K} = \frac{0{\cdot}0201}{0{\cdot}0821 \times 0{\cdot}00089} = 275.$

Mean value of $k_b/K = 276$.

p-Trimethylaminobenzoic Acid (p-Benzbetaine),



This substance was prepared by the action of methyl iodide on either *p*-aminobenzoic acid or its dimethyl derivative.* The iodide was recrystallised from water, and decomposed by the action of moist silver hydroxide *in the cold*. If the mixture is heated, a strongly basic substance is obtained, which has not yet been investigated. The benzbetaine was purified by recrystallisation from absolute alcohol, from which it separated in cubes, melting at 255°:—

Iodine found	41·1 per cent.
$C_6H_4<^{COOH}_{N(CH_3)_3I}$ requires I	41·4 „

Determination of Basic Constant—Catalysis Method.

0·307 gramme iodide in 15 c.c. water, 1 c.c. MeAc, $v = 15$, $A = 15{\cdot}40$.

I.

t.	Titre.	*x.*	A−*x.*	*c.*
0	1·20	0	15·40	—
2,755	2·52	1·32	14·08	0·0000142
4,160	3·14	1·94	13·46	141
5,665	3·90	2·70	12·70	148
7,035	4·53	3·33	12·07	150
8,505	5·12	3·92	11·48	150
10,055	5·80	4·60	10·80	153
12,788	6·78	5·58	9·82	153
			Mean	0·0000148

* Compare Michael and Wing, 'Amer. Chem. Journ.,' vol. 7, p. 195, 1885.

II.

t.	Titre.	x.	$A-x$.	c.
0	1·22	0	15·40	—
2,690	2·56	1·34	14·06	0·0000147
5,708	3·90	2·68	12·72	145
8,441	5·05	3·83	11·57	147
9,871	5·64	4·42	10·98	149
11,361	6·12	4·90	10·50	146
			Mean	0·0000147

N/15 Cl solution (5 per cent. HCl, 95 per cent. KCl), $c = 0{\cdot}0000102$.

From I— $$\frac{k_b}{K} = \frac{0{\cdot}9275 \times 15}{(0{\cdot}0725)^2} = 2650.$$

And from II— $$\frac{k_b}{K} = \frac{0{\cdot}928 \times 15}{(0{\cdot}072)^2} = 2685.$$

Mean for $k_b/K = 2667$.

Determination of the Acidic Constant—Salt Hydrolysis.

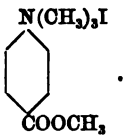
A.—25 c.c. N/16 NaOH, 25 c.c. MeAc, 50 c.c. water.

B.—As A, but with 0·308 gramme *p*-benzbetaine added.

t.	Titre.	x.	t.	Titre.	x.
0	12·40	0	0	12·40	0
11	4·20	8·20	11	4·30	8·10
13	3·70	8·70	13	3·80	8·60
15	3·27	9·13	15	3·40	9·0
18	2·90	9·50	17	3·10	9·30

It is here evident that reaction B proceeded almost as quickly as reaction A, a fact which shows that the sodium salt of *p*-benzbetaine is almost entirely hydrolysed in N/64 solution. Now if 4 per cent. remained unhydrolysed, that would correspond to a value of k_a/K less than 3; so it may with certainty be stated that the value of k_a cannot be greater than 10^{-14}.

The smallest value of k_a deduced from conductivity measurements lay between 10^{-7} and 10^{-8}; it was, therefore, useless to attempt the further purification of the substance by crystallisation, on account of its great solubility and its small inherent conductivity.

p-Benzbetaine Ester Iodide, 

This salt was prepared by heating equivalent quantities of methyl iodide and the methyl ester of *p*-dimethylaminobenzoic acid at 100° for five hours in a sealed tube. On cooling and opening the tube, the mixture was extracted with water. After filtration, the aqueous solution was evaporated down, when the iodide separated. Colourless crystals were obtained by recrystallisation from aqueous alcohol:—

Iodine found	38·8 per cent.
$C_6H_4<^{N(CH_3)_3I}_{COOCH_3}$ requires I	39·6 „

A decinormal solution had an acid reaction to azolitmin, but did not affect methyl orange or congo red.

The catalytic action of an aqueous solution of the iodide on methyl acetate was too slow to yield a definite value for the basic constant of the substance.

Methyl Ester of Glycine, $NH_2.CH_2.COOCH_3$.

This was prepared in an analogous manner to the other methyl esters. On cooling, crystals of the hydrochloride separated in the form of white plates. After recrystallisation from methyl alcohol, the hydrochloride melts at 175° to 176° with decomposition.

Chlorine found.....	28·42 per cent.
$NH_2.CH_2.COOCH_3.HCl$ requires Cl	28·29 „

Determination of Basic Constant—Catalysis Method.

I.

0·397 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 4·7$.

t.	Titre.	*x.*	*c.*
0	0·30	0	—
7,040	2·55	2·25	0·0000104
9,910	3·65	3·35	110
12,825	4·75	4·45	113
15,880	5·90	5·60	113
17,495	6·65	6·35	116
		Mean	0·0000111

II.

0·462 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 4·1$.

t.	Titre.	x.	c.
0	0·20	0	—
5,585	1·95	1·75	0·0000101
8,498	3·10	2·90	110
11,553	4·30	4·10	113
13,168	4·95	4·75	116
		Mean	0·0000111

N/15 Cl solution (5 per cent. HCl, 95 per cent. KCl), $c = 0·0000104$.

From I— $$\frac{k_b}{K} = \frac{0·983 \times 4·7}{0·0167^2} = 16,500.$$

And from II— $$\frac{k_b}{K} = \frac{0·985 \times 4·1}{0·0146^2} = 18,900.$$

Mean value for $k_b/K = 18,000$ (?).

In these experiments nitrophenol was found to be the best indicator, but was not satisfactory.

Ethyl Ester of Glycine, $NH_2.CH_2.COOC_2H_5$.

A specimen of the hydrochloride obtained from Kahlbaum was recrystallised from absolute alcohol.

Chlorine found ..... 25·20 per cent.
$NH_2.CH_2.COOC_2H_5.HCl$ requires Cl ..... 25·45 „

A methyl acetate catalysis experiment with the hydrochloride showed that the ethyl ester of glycine was a stronger base than the methyl ester, but the action proceeded too slowly to admit of an accurate calculation of the basic constant.

Dimethylglycine, $N(CH_3)_2.CH_2.COOH$.

This substance was prepared according to the method given by Eschweiler.* Equivalent quantities of a 33-per-cent. aqueous solution of dimethylamine and of formaldehyde-cyanhydrin were mixed. After standing for 24 hours the resulting nitrile was extracted with ether, and, after removal of the ether, was saponified with baryta. The barium was removed by means of carbonic anhydride, and the solution was evaporated to dryness. The residue was dissolved in absolute alcohol, from which it afterwards separated in exceedingly hygroscopic crystals, which melted at 157° to 160°.

* 'Liebig's Annalen,' vol. 279, p. 44, 1894.

0·2080 gramme gave ammonia equivalent to 0·0278 gramme N ..... 13·36 per cent.
$N(CH_3)_2CH_2.COOH$ requires N ..... 13·60 „

A sample of the hydrochloride was prepared by treating with hydrochloric acid. On recrystallising it from alcohol, it was obtained in the form of white hygroscopic crystals, melting at 190° with decomposition.

0·192 gramme gave ammonia equivalent to 0·0192 gramme N ..... 10·0 per cent.
Chlorine found ..... 25·28 „
$N(CH_3)_2.CH_2.COOH.HCl$ requires N = 10·0, Cl ... 25·45 „

Determination of Basic Constant—Catalysis Method.

I.

0·207 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 10·1$, A = 15·40.

t.	Titre.	*x.*	A−*x.*	*c.*
0	1·85	0	15·40	—
1167	4·96	3·11	12·29	0·0000840
1535	5·80	3·95	11·45	839
2996	8·60	6·75	8·65	836
3996	10·10	8·25	7·15	834
6924	13·20	11·35	4·05	838
			Mean	0·0000837

N/15 Cl solution (45 per cent. HCl, 55 per cent. KCl), $c = 0·0000881$.

$$\frac{k_b}{K} = \frac{0·712 \times 10·1}{0·288^2} = 87.$$

II.

0·188 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 11·13$, A = 15·40.

t.	Titre.	*x.*	A−*x.*	*c.*
0	1·80	0	15·40	—
1238	4·78	2·98	12·42	0·0000754
3742	9·26	7·46	7·94	769
3947	9·60	7·80	7·60	777
4178	9·96	8·16	7·24	784
5200	11·20	9·40	6·00	787
			Mean	0·0000774

N/15 Cl solution (40 per cent. HCl, 60 per cent. KCl), $c = 0·0000774$.

$$\frac{k_b}{K} = \frac{0·703 \times 11·13}{0·297^2} = 89.$$

In II the temperature of the thermostat increased slightly during the course of the reaction; the comparison solution was going simultaneously, and was similarly affected.

Mean value of $k_b/K = 88$.

Determination of the Acidic Constant.—The conductivity method was tried, but, owing to the very slight conducting power and to the difficulties attending recrystallisation, it gave too high results; the smallest value of k_a obtained by this means was 2×10^{-7}.

Shields' Method.

0·161 gramme dimethylglycine, 25 c.c. N/16 soda, 10 c.c. MeAc solution,

$$E = \frac{1}{v} = 0{\cdot}0446.$$

t.	Titre.	x.	E$-x$.	kc.
0	8·70	0	0·0446	—
110	5·75	0·0147	0·0299	0·00084
148	5·35	0·0167	0·0279	89
172	5·15	0·0177	0·0269	89
307	4·45	0·0212	0·0234	86
			Mean	0·00087

Whence

$$\frac{k_a}{K} = \frac{k}{kc} = \frac{10{\cdot}5}{0{\cdot}00087} = 1{\cdot}21 \times 10^4, \quad \text{and} \quad k_a = 1{\cdot}4 \times 10^{-10}.$$

Trimethylglycine (Betaine), $\overline{\text{N}(CH_3)_3.CH_2.COO}$.

Betaine hydrochloride was obtained by the saponification of betaine ethyl ester hydrochloride, which was effected by boiling for four hours with dilute hydrochloric acid. After partial evaporation of the water, beautiful white crystals of betaine hydrochloride separated out, and were dried in a desiccator:—

Chlorine found	23·15 per cent.
$N(CH_3)_3.CH_2.COO.HCl$ requires Cl.....	23·12 „

Determination of the Basic Constant—Catalysis Method.

I.

0·228 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 10·1$, $A = 15·40$.

t.	Titre.	x.	$A-x$.	c.
0	1·75	0	15·40	—
1425	5·72	3·97	11·43	0·0000909
2595	8·17	6·42	8·98	902
2745	8·44	6·69	8·71	902
2880	8·71	6·96	8·44	907
3060	9·03	7·28	8·12	908
3876	10·31	8·56	6·84	909
			Mean	0·0000906

II.

0·271 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 8·5$, $A = 15·40$.

t.	Titre.	x.	$A-x$.	c.
0	2·20	0	15·40	—
1443	6·50	4·30	11·10	0·0000986
1560	6·78	4·58	10·82	983
2562	8·99	6·79	8·61	986
2646	9·17	6·97	8·43	989
			Mean	0·0000986

N/15 Cl solution (45 per cent. HCl, 55 per cent. KCl), $c = 0·0000875$.

Whence from I— $$\frac{k_b}{K} = \frac{0·686 \times 10·1}{0·314^2} = 70,$$

and from II— $$\frac{k_b}{K} = \frac{0·713 \times 8·5}{0·287^2} = 73.$$

Mean value for $k_b/K = 72$.

Bredig* from the electrical conductivity calculated the value $k_b/K = 63$.

Determination of the Acidic Constant.—In carrying this out, the hydrochloride was used along with two equivalents of soda, on account of the difficulty in obtaining pure betaine. This, however, answered the purpose equally well, for Shields states that the presence of a neutral salt exerts practically no influence on the velocity of the reaction :—

* 'Zeit. physikal. Chem.,' vol. 13, p. 323, 1894.

A.—25 c.c. N/16 NaOH, 25 c.c. N/16 MeAc, 50 c.c. water.

B.—0·241 gramme betaine hydrochloride, 50 c.c. N/16 NaOH, 25 c.c. N/16 MeAc, 25 c.c. water.

t.	Titre.	*x.*	*t.*	Titre.	*x.*
0	12·40	0	0	12·40	0
5	6·50	5·90	5	6·50	5·90
11	4·20	8·20	11	4·35	8·05
13	3·70	8·70	13	3·75	8·65
15	3·27	9·13	15	3·35	9·05

As in the case of *p*-benzbetaine, it is evident that k_a cannot exceed 10^{-14}.

$N(CH_3)_3Cl.CH_2.COOC_2H_5$, *Betaine Ethyl Ester Chloride.*

This salt was prepared by adding an equivalent of methyl chloracetate to a solution of trimethylamine in absolute alcohol. After standing some time the alcohol was partially evaporated off, and on cooling, the substance separated out as white extremely hygroscopic crystals, which melted at 143° to 144°, with decomposition :—

0·2165 gramme gave ammonia equivalent to 0·0159 gramme N	7·35 per cent.
Chlorine found	19·67 „
$N(CH_3)_3Cl.CH_2.COOC_2H_5$ requires N = 7·71, Cl ...	19·55 „
$N(CH_3)_3Cl.CH_2.COOCH_3$ „ N = 8·36, Cl ...	21·20 „

The substance by its composition and melting-point was thus proved to be the ethyl ester chloride, the formation of which was due to the choice of ethyl alcohol as solvent.*

Determination of Basic Constant—Catalysis Method.

I.

0·315 gramme substance in 15 c.c. water, 1 c.c. MeAc, v = 8·64, A = 15·40.

t.	Titre.	*x.*	A−*x.*	*c.*
0	0·12	0	15·40	—
11,117	3·65	3·53	11·87	0·0000102
12,564	4·02	3·90	11·50	101
14,072	4·50	4·38	11·02	103
15,583	5·00	4·88	10·52	106
16,868	5·33	5·21	10·19	106
			Mean	0·0000103

* Compare Koeppen, 'Berichte,' vol. 38, p. 167, 1905.

II.

0·2945 gramme substance in 15 c.c. water, 1 c.c. MeAc, $v = 9{\cdot}24$, $A = 15{\cdot}40$.

t.	Titre.	x.	$A-x$.	c.
0	0·13	0	15·40	—
9,790	3·35	3·22	12·18	0·0000104
11,243	3·80	3·67	11·73	105
12,751	4·30	4·17	11·23	107
14,262	4·76	4·63	10·77	109
15,547	5·17	5·04	10·36	110
			Mean	0·0000107

N/15 Cl solution (5 per cent. HCl, 95 per cent. KCl), $c = 0{\cdot}0000102$.

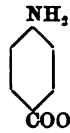
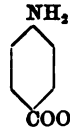
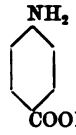
From I— $$\frac{k_b}{K} = \frac{0{\cdot}97 \times 8{\cdot}64}{0{\cdot}0290^2} = 9900.$$

And from II— $$\frac{k_b}{K} = \frac{0{\cdot}968 \times 9{\cdot}24}{0{\cdot}0323^2} = 8600.$$

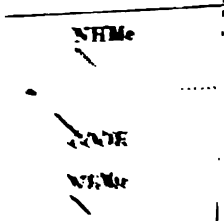
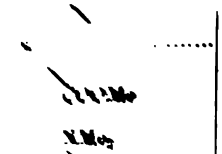
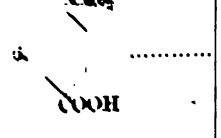
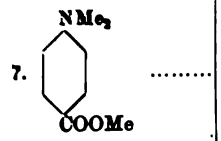
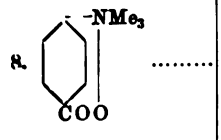
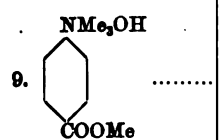
Mean value for $k_b/K = 9000$.

This value can only be regarded as approximate, owing to the length of time over which the action extended.

Summary of Results.

	k_a.	k_a/K.	k_b.	k_b/K.
*1. 	$1{\cdot}21 \times 10^{-5}$	1×10^9	$2{\cdot}54 \times 10^{-12}$	210
2. 	—	—	$2{\cdot}42 \times 10^{-12}$	200
3. 	—	—	$2{\cdot}88 \times 10^{-12}$	238

* The values pertaining to the substances marked with an asterisk are derived from Winkelblech's measurements (*loc. cit.*), and, except in the case of *p*-aminobenzoic acid, are not strictly comparable with my results.

	k_a.	k_a/K.	k_b.	k_b/K.
	$0{\cdot}92 \times 10^{-5}$	$0{\cdot}76 \times 10^{9}$	$1{\cdot}66 \times 10^{-12}$	137
	—	—	$2{\cdot}08 \times 10^{-12}$	173
	$0{\cdot}94 \times 10^{-5}$	$0{\cdot}778 \times 10^{9}$	$3{\cdot}25 \times 10^{-12}$	269
7. 	—	—	$3{\cdot}34 \times 10^{-12}$	276
8. 	*ca.* 10^{-14}	—	$3{\cdot}23 \times 10^{-11}$	2667
9. 	—	—	Very great	Very great
*10. $CH_2<^{NH_2}_{COOH}$	$3{\cdot}4 \times 10^{-10}$	28,100	$2{\cdot}94 \times 10^{-12}$	243
11. $CH_2<^{NH_2}_{COOMe}$	—	—	$2{\cdot}2 \times 10^{-10}$	18,000
*12. $CH_2<^{NHMe}_{COOH}$	$1{\cdot}3 \times 10^{-10}$	10,750	$1{\cdot}77 \times 10^{-12}$	146
13. $CH_2<^{NMe_2}_{COOH}$	$1{\cdot}4 \times 10^{-10}$	12,000	$1{\cdot}06 \times 10^{-12}$	88
14. $CH_2<^{NMe_3}_{COO}$	*ca.* 10^{-14}	—	$8{\cdot}7 \times 10^{-13}$	72
15. $CH_2<^{NMe_2OH}_{COOEt}$	—	—	11×10^{-11}	9000 (?)

* The values pertaining to the substances marked with an asterisk are derived from Winkelblech's measurements (*loc. cit.*), and, except in the case of *p*-aminobenzoic acid, are not strictly comparable with my results.

The Affinity Constants of Amphoteric Electrolytes. II.—*Methyl Derivatives of Ortho- and Meta-aminobenzoic Acids.*

By ALEXANDER CHARLES CUMMING, D.Sc. (1851 Exhibition Scholar).

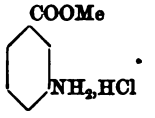
(Communicated by Professor James Walker, F.R.S. Received May 21,—Read May 31, 1906.)

(From the Chemical Laboratory, University College, Dundee.)

The investigation by Winkelblech* of various amphoteric electrolytes, and the subsequent application to his experimental figures of the theory of electrolytic dissociation and the law of mass action,† showed that the aminobenzoic acids exhibit their amphoteric character in a marked manner.

The following paper contains the results of an investigation of the methyl derivatives of ortho- and meta-aminobenzoic acids undertaken to ascertain the effect of successive introductions of a methyl group on the strength of these substances both as acids and as bases.

In order to obtain all the possible methyl derivatives of *m*-aminobenzoic acid and of anthranilic acid, it was found necessary to prepare several new substances and to revise some previous work. Since this portion of the research is only incidentally connected with the more physical part, it has been kept separate, and placed before the account of the physico-chemical measurements.

Hydrochloride of Methyl Ester of m-Aminobenzoic Acid, 

The following method of preparation was found by trial to give good yields and was used throughout in the preparation of the esters and their hydrochlorides of both the ortho and meta series. Dry hydrogen chloride was passed through a boiling methyl alcoholic solution of the acid, which was contained in a flask fitted with an inverted condenser. On cooling the solution, it was found that the ester hydrochloride usually separated in crystals. In some instances crystals separated when the hydrogen chloride had passed for a few minutes, but this was due to the insolubility of the hydrochloride of the acid, and as the action progressed these crystals dissolved again.

When the hydrochloride of the ester proved to be soluble in alcohol, it was necessary to concentrate the solution before crystals would separate. The

* 'Zeit. f. physikal. Chem.,' vol. 36, p. 546, 1901.

† Walker, 'Roy. Soc. Proc.,' vol. 73, p. 155, and vol. 74, p. 271.

esters of the meta series formed much more slowly than those of the ortho series.

A convenient method of finding roughly how far the action had gone at any time was to take a small sample of the solution, boil off most of the hydrochloric acid, and then add some aqueous solution of sodium acetate, which caused the ester to separate as an oil. If the acid was insoluble, it also was precipitated.

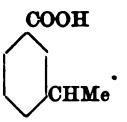
The hydrochloride of the methyl ester of *m*-aminobenzoic acid was made in this manner, and the action was found to be complete at the end of five hours. The crystals melted at 201° to 202°, with decomposition, and the melting point remained the same after two crystallisations from alcohol.

The amount of chloride in the recrystallised salt was estimated with the following result:—

0·1880 gramme of the salt contained 0·0389 gramme chlorine.

Found Cl	20·16 per cent.
Calculated for $C_8H_{10}O_2NCl$.....	20·46 „

The methyl ester of *m*-aminobenzoic acid separated as a fragrant oil when sodium acetate solution was added to a solution of the hydrochloride.

Monomethyl m-Aminobenzoic Acid, 

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Equivalent quantities of *m*-aminobenzoic acid and methyl iodide were heated together in a sealed tube for about three hours at 100°, when it was found that combination had occurred, the resulting compound being the hydriodide of monomethyl *m*-aminobenzoic acid. This was crystallised from alcohol to remove any of the original acid, and appeared as a white crystalline substance, which melted with decomposition at 215°, and was soluble in hot water and alcohol, but much less so in the cold solvents. It did not crystallise well from water, as it underwent slight decomposition.

Estimation of the iodine present resulted as follows:—

0·2790 gramme of the substance contained 0·1253 gramme iodine.

Iodine found	44·9 per cent.
Calculated for $C_8H_{10}O_2NI$.....	45·3 „

The iodide dissolved readily in aqueous potash, and on addition of acetic acid, monomethyl *m*-aminobenzoic acid separated in small crystals, which, after crystallisation from water, were free from colour and melted at 147°. (The dimethyl acid melts at 151°.)

Estimation of the nitrogen by Kjeldahl's method gave the following results:—

0·143 gramme contained 0·0133 gramme of nitrogen..... 9·30 per cent.
0·147 „ „ 0·0135 „ „ ..... 9·21 „

Calculated for $C_8H_9O_2NI$ ..... 9·30 per cent.

The substance was acid to litmus and to phenolphthalein.

0·1180 gramme neutralised with phenolphthalein as indicator 15·90 c.c. of 0·0500 N sodium hydroxide.

The combining weight calculated from these figures is 149, while that required for the formula $C_8H_9O_2N$ is 151.

Monomethyl *m*-aminobenzoic acid was found to be very soluble in alcohol, chloroform, and acetone when hot, but much less so in the cold. It was somewhat soluble in hot water and almost insoluble in cold water, ether, and ligroin; soluble in dilute mineral acids, but not in acetic acid.

The same substance was also prepared in the following manner, though the yield in this case was very small, on account of the number of operations. When an aqueous solution of the sodium salt of *m*-aminobenzoic acid was treated with an equimolecular amount of methyl sulphate, an orange-coloured acid substance was obtained which melted at about 145°, and retained the same melting point and appearance after crystallisation from several solvents.

Analyses showed that this was a mixture of the mono- and di-methyl acids, and variations in the method of preparation failed to give a pure product, whilst numerous attempts at separation by crystallisation were also unsuccessful.

The substitution of methyl iodide for methyl sulphate also yielded an orange-coloured substance, which, as far as it was examined, appeared to be the same mixture. The mixture was separated into its components by methylation with boiling methyl alcohol and dry hydrochloric acid, when the hydrochlorides of the methyl esters of the respective acids were formed. These were readily separated, as the hydrochloride of the methyl ester of monomethyl *m*-aminobenzoic acid is insoluble in cold alcohol, while that of the dimethyl acid is very soluble.

The two hydrochlorides obtained in this way possessed the same properties as those of the mono- and di-methyl acid esters made by other methods, as described below.

The monomethyl *m*-aminobenzoic acid was readily prepared from its ester hydrochloride by boiling with excess of aqueous caustic soda. The addition of acetic acid to the solution thus obtained precipitated the monomethyl

m-aminobenzoic acid, which does not form an acetate stable in aqueous solution. The acid so prepared was quite free from any pink colour.

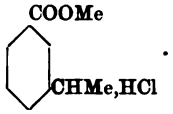
P. Griess* obtained a pink substance from *α*-benzcreatine, and described it as monomethyl *m*-aminobenzoic acid, but he gave neither analysis nor melting point.

The result of the work detailed above indicates that Griess' substance was probably a mixture, since the coloured substance which I obtained was proved to be a mixture, although both mono- and di-methyl *m*-aminobenzoic acids are free from colour when pure.

It was found that this pink colour could be produced by boiling a solution made from a mixture of the pure, colourless monomethyl and dimethyl acids, though on one occasion, for some unknown reason, the resulting colour was green. It is probable that the colour is due to oxidation.

From the failure to effect a separation of the mixture by crystallisation it was considered that the solubilities of the two acids in the various solvents tried must be very similar, and by experiment with the pure substances it was found that this was the case, the list of solubilities for the dimethyl acid being exactly the same as that given above for monomethyl *m*-amino-benzoic acids.

Hydrochloride of the Methyl Ester of Monomethyl m-Aminobenzoic Acid,



After treatment of a boiling methyl alcohol solution of monomethyl *m*-aminobenzoic acid with dry hydrogen chloride for four hours, crystals separated on cooling.

These were dried on tile, and found to melt at 75° to 78°. It must be mentioned that none of the melting points given for these hydrochlorides are true melting points, but are more or less definite decomposition temperatures. Estimation of the chloride present resulted as follows:—

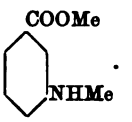
0·2010 gramme of the salt contained 0·0354 gramme chlorine.

Chlorine found.....	17·61 per cent.
Calculated for $C_9H_{12}O_2NCl$.....	17·62 „

This hydrochloride was also prepared, as previously described, as a step in the preparation of monomethyl anthranilic acid. It can also be readily made from the ester by passing dry hydrochloric acid through an ethereal solution of

* 'Berichte,' vol. 8, p. 325.

the ester. However prepared, it is unstable, as it loses hydrochloric acid by simple exposure to the air.

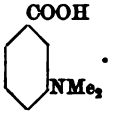
Methyl Ester of Monomethyl m-Aminobenzoic Acid, 

This substance was prepared by washing its hydrochloride with water, whereby all the hydrochloric acid was removed and the ester obtained as a white solid.

The methyl ester of monomethyl *m*-aminobenzoic acid was found to possess a faint pleasant odour, and was obtained in good crystals by slow evaporation of its ethereal solution. It was very soluble in ether, slightly soluble in alcohol, and extremely insoluble in water.

It melted at 72°, and thus differed in a marked manner from the esters of *m*-aminobenzoic acid and of the dimethyl acid, since both of these are oils.

The preparation of this ester and its hydrochloride in another way has been described under the preparation of monomethyl *m*-aminobenzoic acid.

Dimethyl m-Aminobenzoic Acid, 

The orange-coloured mixture, obtained, as previously described (p. 105), by the action of methyl sulphate and caustic soda on *m*-aminobenzoic acid, was dissolved in just sufficient aqueous sodium hydroxide and again treated with methyl sulphate. The resulting crystalline precipitate was free from any pink colour, and proved to be dimethyl *m*-aminobenzoic acid. The yield was 30 per cent. of the calculated quantity, but could probably be much increased, since no attempt was made to find the best conditions. The separation of the dimethyl acid from the orange-coloured mixture by means of its methyl ester hydrochloride has already been described under monomethyl *m*-aminobenzoic acid. This method involved too many operations to give other than a very small yield.

P. Griess* prepared this acid from its methyl ester, which he obtained by melting *m*-benzbetaine; a quantity was prepared in this way according to his directions.

Another new method of preparing dimethyl *m*-aminobenzoic acid was discovered after sufficient for use had been obtained by the above three methods, but it appeared to be the easiest method of preparation.

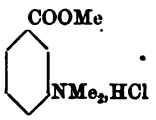
Some hydrochloride of *m*-benzbetaine was cautiously melted, when hydrochloric acid was evolved, and a yellow oil, the methyl ester of dimethyl

* 'Berichte,' vol. 6, p. 587.

m-aminobenzoic acid, remained behind. From the ester, the acid was readily prepared by boiling for a few minutes with potash solution, and then adding acetic acid, when the dimethyl acid separated in small crystals. As the hydriodide of *m*-benzbetaine proved to be one of the easiest derivatives to prepare, the same action was then tried with it. Like the hydrochloride, it also yielded the ester of the dimethyl acid on heating.

The samples obtained by the above methods were each found to agree with Griess' description.

Hydrochloride of the Methyl Ester of Dimethyl m-Aminobenzoic Acid,



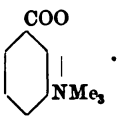
Some *m*-benzbetaine was placed in a tube in a metal bath and the tube exhausted. The temperature was kept at 150°, until all the water from the deliquescent betaine was removed, and was then raised for 15 minutes to 220°, at which temperature Griess showed* that *m*-benzbetaine changes into the isomeric methyl ester of dimethyl *m*-aminobenzoic acid.

The ester was dissolved in ether, and dry hydrochloric acid was passed through the solution. The resulting crystalline precipitate, after several washings with ether, was dried on tile. This hydrochloride was found to be a pure white crystalline salt, which melted at 175° to 177°, and contained the following amount of chlorine:—

0·1805 gramme contained 0·0295 gramme of chlorine.

Chlorine found.....	16·04 per cent.
Calculated for $C_{10}H_{14}O_2NCl$	16·45 „

m-Benzbetaine,



m-Aminobenzoic acid was dissolved in 50-per-cent. methyl alcohol and to the solution were added three equivalents of methyl iodide, together with one equivalent of potassium hydroxide. The solution was then allowed to stand for several days, with addition of more potash whenever it was found to have become acid, until three equivalents of potash had been used.

Thus far the method used was similar to that employed to obtain *p*-benzbetaine, by Michael and Wing,† but the subsequent treatment was different.

* *Loc. cit.*

† 'Amer. Chem. Journ.,' vol. 7, pp. 196—7.

Michael and Wing first evaporated the solution to dryness, and then went through several operations to remove the potassium iodide, after which the betaine was precipitated as the hydriodide by addition of hydriodic acid.

The method I adopted was to concentrate the solution sufficiently to remove most of the alcohol, and then add a little acetic acid to precipitate any mono- or di-methyl acid present. After filtration, hydrochloric acid was added, whereby all the *m*-benzbetaine present was precipitated as hydriodide, since the solution contained plenty of potassium iodide.

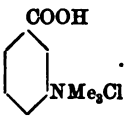
The *m*-benzbetaine hydriodide was found to be almost entirely free from chloride, methiodide and periodide, and was readily purified by crystallisation from water. It melted at 180°, and estimation of the iodine present gave the following result:—

0·3925 gramme of the iodide contained 0·1605 gramme of iodine.

Iodine found	40·90 per cent.
Calculated for $C_{10}H_{14}O_2NI$	41·36 „

m-Benzbetaine was prepared from the hydriodide by treatment with moist silver oxide or lead hydroxide, and was purified by several crystallisations from alcohol. It was very deliquescent, and at 215° to 220° was transformed into the methyl ester of dimethyl *m*-aminobenzoic acid.*

o-Benzbetaine was successfully obtained by the use of the same process, so it may be of general applicability in the preparation of benzbetaines.

Hydrochloride of m-Benzbetaine, 

This was prepared by mixing the betaine with concentrated hydrochloric acid. The salt is almost insoluble in concentrated hydrochloric acid and only slightly soluble in water. It was found to be white and not deliquescent; it melted at 192°, and contained the following amount of chlorine:—

0·1940 gramme contained 0·0298 gramme of chlorine.

Chlorine found.....	15·35 per cent.
Calculated for $C_{10}H_{14}O_2NCl$ ...	16·45 „

The hydrochloride was recrystallised from alcohol, and the chlorine again estimated:—

0·1880 gramme contained 0·0285 gramme of chlorine.

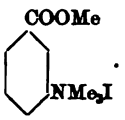
Chlorine found.....	15·18 per cent.

* Griess, *loc. cit.*

The hydrochloride was then suspended in alcohol and dry hydrochloric acid led through. The crystals were then filtered off, and dried on a tile, not in a desiccator :—

0·198 gramme contained 0·0324 gramme of chlorine.
Chlorine found..... 16·36 per cent.

This sample was used at once in a catalysis experiment, as it contained the right proportion of chlorine.

Methiodide of the Methyl Ester of Dimethyl m-Aminobenzoic Acid, 

This substance was readily obtained by the action of methyl iodide on the methyl ester of dimethyl *m*-aminobenzoic acid, as described by Willstätter and Kahn.* These authors drew attention in their paper to the ease with which betaines of this class yielded, by internal rearrangement, the isomeric methyl ester of the dimethyl acid, and showed this property to be well marked in the case of *m*-benzbetaine. In this connection the following new mode of obtaining the quaternary iodide is of some interest, though it offers no advantages as a method of preparation :—

Some dry *m*-benzbetaine was kept in a closed tube with methyl iodide at 30° to 40° for 24 hours, when it was found that most of the betaine had been used up with formation of the quaternary iodide. That this reaction is simply a combination of the betaine with methyl iodide does not seem probable. It is more probable that the change of *m*-benzbetaine into the ester proceeds even at low temperatures, but reaches an equilibrium, unless the ester is removed as it is formed. In this case we know that methyl iodide combines quickly and readily with the methyl ester of *m*-amino-benzoic acid. The ester would thus be removed as it was produced, and the reaction would therefore proceed steadily to completion. The application of this hypothesis to the similar ortho compounds would require the reaction between *o*-benzbetaine and methyl iodide to proceed much more slowly, as the interaction of the methyl ester of dimethyl anthranilic acid and methyl iodide is known to be very slow. By experiment it was found that only a small yield of the quaternary ortho iodide was obtained when a mixture of methyl iodide and *o*-benzbetaine had been kept in a warm place for two weeks.

* 'Berichte,' p. 411, 1904.

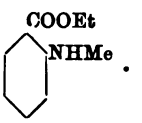
Preparation of the Ortho-aminobenzoic Acid Series.

All the methyl derivatives of this series have been described, and the samples used were prepared mainly by the methods of Willstätter and Kahn.*

There is a slight ambiguity in a passage of their paper which conveys the impression that the compound which they obtained by the action of methyl sulphate on anthranilic acid was the methyl ester of monomethyl-anthranilic acid instead of the acid itself. It may be mentioned that in an abstract of their paper† it is stated that they obtained the methyl ester in this way and not the acid. To prevent the possibility of any mistake, the substance, prepared according to their directions, was analysed, with the following result:—

0·2120 gramme of the substance gave on combustion 0·1165 gramme of water and 0·4935 gramme of carbon dioxide.

Found	C = 63·49, H = 6·10
Calculated for monomethyl-anthranilic acid	C = 63·57, H = 5·96

Ethyl Ester of Monomethyl-anthranilic Acid, 

.

This was prepared from monomethyl-anthranilic acid by the action of boiling ethyl alcohol and hydrogen chloride for 10 hours. The solution was evaporated almost to dryness, and then excess of dilute caustic soda was added, whereby the ester separated as an oil, which was removed by extraction with ether. The ethereal solution was washed with dilute alkali, dilute hydrochloric acid, and then several times with water, after which the ether was evaporated.

The ethyl ester of monomethyl-anthranilic acid was found to be a colourless oil with a pleasant odour of jasmine. It was solid below 18° to 20°, and, therefore, closely resembled the methyl ester in both odour and melting point. It was somewhat soluble in alcohol, freely soluble in ether, and so extremely insoluble in water and acids that it was not found possible to determine its strength as a base.

The hydrochloride was prepared as a white crystalline salt by passing dry hydrogen chloride into a solution of the ester. It was soluble in alcohol, insoluble in ether, and mixing it with water caused an instantaneous

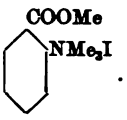
* 'Berichte,' p. 401, 1904.

† 'Chem. Soc. Journ.,' 86, I, p. 235, 1904.

separation of the ester from the hydrochloric acid. Analysis of the amount of chlorine present gave this result :—

0·1890 gramme of the hydrochloride contained 0·0312 gramme of chlorine.

Found chlorine	16·50.
Calculated for $C_{10}H_{14}O_2NCl$	16·45.

Methiodide of the Methyl Ester of Dimethyl-anthranilic Acid, 

This compound was prepared in the manner recommended by Willstätter and Kahn,* namely, by the interaction of methyl iodide and the methyl ester of dimethyl-anthranilic acid, and it was found that the yield became almost theoretical if the mixture was kept for many days at about 40°.

The above authors state that this combination does not occur in ethereal solution, but this is not strictly correct, as the action does take place, though with extreme slowness. Ether, however, is a poor solvent for the purpose, and it was found that if alcohol or acetone were employed, the rate of reaction approximated to that observed in the absence of any solvent. However, as a method of preparation it is best to use no solvent.

Determination of the Acid and Basic Constants.

Except where it is specifically stated that some other temperature was employed, the experiments detailed in the following pages were performed in a thermostat, which was kept at 25° to within one-tenth of a degree.

Basic Constants.—There are a number of methods available for the determination of the strength of weak bases, and of these the methyl acetate catalysis method was found to be the most generally applicable. The comparison method, details of which may be found in the paper of Walker and Wood,† was employed as being the most accurate and, as the figures below will show, these amphoteric electrolytes gave as good results as those obtainable with ordinary electrolytes.

As a general rule the hydrochloride was used, but in a few cases the hydriodide was more readily prepared in a state of purity and was therefore substituted for the chloride. One might naturally expect the hydrolysis of a chloride and of an iodide to be equal, but as there was no experimental evidence as to the action of hydriodic acid and iodides on methyl acetate a few experiments were tried.

* *Loc. cit.*

† 'Chem. Soc. Journ.,' vol. 83, p. 484.

Solutions were prepared, one of which was N/200 for hydrochloric acid and N/10 for potassium chloride, while the other was N/200 for hydriodic acid and N/10 for potassium iodide. The experiments were performed in duplicate, and the constant found for the chloride solution was 0·00080 as against 0·00053 for the iodide. Both acids were standardised in the same manner and against the same soda solution. To eliminate any error in determining the strength of the acids, the following experiments were next performed:—

Solution A was made from 10 c.c. of N/10 hydrochloric acid, 1·5 grammes of potassium chloride, and 10 c.c. of water, and was, therefore, N/20 for acid and N for total chloride.

c found = 0·000158.

Solution B was made from 10 c.c. of N/10 hydrochloric acid, 2·38 grammes of potassium bromide, and 10 c.c. of water, and was, therefore, N/20 for acid and N for total bromide contents.

c found = 0·000160.

Solution C was made from 10 c.c. of N/10 hydrochloric acid, 3·3 grammes of potassium iodide, and 10 c.c. of water, and was, therefore, N/20 for acid and N for total iodide contents.

c found = 0·000140.

Since an equal quantity of the same acid was used in all cases, the difference can only be due to the difference between chloride and iodide. It will be noticed that the bromide and chloride agree, and that the error arising from the use of an iodide is that too low a value is obtained for the hydrolysis, and consequently too high a value for k_b/K. The cause is most probably oxidation of the hydriodic acid, since the solution, which at the start was almost colourless, always darkened during the experiment.

Other methods for determining the basic constant were also tried, but were mostly unsatisfactory on account of the readiness with which the substances oxidise in solution.

Acid Constants.—In some cases an attempt was made to determine the acid dissociation constant by direct measurement of the hydrion concentration by the interesting new method of Bredig and Fraenkel,* who have found that extremely small concentrations of hydrion can be measured by the rate at which the catalysis of diazo-acetic ester occurs. Details of the method as applied in this research will be found under anthranilic acid (*o*-amino-benzoic acid).

The acid dissociation constants for the stronger acids were obtained by

* 'Zeit. Elektrochem.,' vol. 2, p. 525, 1905.

calculation from the conductivities by Walker's method. As most of these substances possess a tendency to oxidise in solution, the conductivity was always determined in a cell with unplatinised electrodes, but as they are all feeble electrolytes, this did not diminish the accuracy of the readings.

The water used for the conductivities was prepared as recommended by Walker and Cormack,* and none was used with a conductivity greater than $1{\cdot}5 \times 10^{-6}$ at 25°.

The sodium hydroxide used in the preparation of the sodium salts was made by exposing metallic sodium to a wet atmosphere in a vessel protected from the atmosphere until it was completely hydrated, and the hydroxide was then dissolved in pure "conductivity" water. Platinised electrodes were, of course, available for the sodium salts.

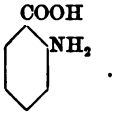
Saponification of Methyl Acetate (Shields' Method).—Where the conductivity of any substance proved too small to be of any use, the strength of the acid was found by the rate at which the sodium salt saponified a methyl-acetate solution.† Several attempts were made to prepare the sodium salts in the solid state to insure that exactly equivalent proportions of acid and base were present. Addition of alcohol and ether precipitated the sodium salt from a strong aqueous solution, but in such a gelatinous form that it was not capable of purification.

Consequently, all the sodium salts mentioned in this paper were prepared by solution of a weighed quantity of acid in a standard solution of pure sodium hydroxide. For a methyl-acetate saponification experiment so much of the acid, sodium hydroxide, and methyl-acetate solutions were mixed as to make the solution the same strength for all constituents. The equation for the reaction is then,

$$kc = \frac{1}{t}\left(\frac{\mathrm{E}}{\mathrm{E}-x} - 1 - \log_e \frac{\mathrm{E}}{\mathrm{E}-x}\right),$$

where E is the initial titre, and x the amount changed in any time t. The constant for sodium hydroxide k in the same units at 25° is about 10·5.

From c we obtain k_a by means of the relation $k_a = \dfrac{1{\cdot}2 \times 10^{-14}}{c}$

Anthranilic Acid, 

Basic Constant and Dilution Law.—It has been assumed that the dilution law for simple bases‡ holds true also for amphoteric electrolytes, but there

* 'Chem. Soc. Journ.,' vol. 77, p. 8, 1900.

† Shields, 'Phil. Mag.,' vol. 35, p. 365, 1893.

‡ Arrhenius, 'Zeit. physikal. Chem.,' vol. 5, p. 16, 1890.

has been no experimental justification by the catalysis method for this assumption. The hydrolysis of the hydrochloride of anthranilic acid was therefore determined at several dilutions, by the comparative methyl acetate catalysis method of Walker and Wood.*

If the dilution law is true, then the ratio k_b/K should be the same, whatever the dilution at which the experiment is performed, since by this law the following formula holds true for all dilutions:—

$$\frac{(\text{free acid}) \times (\text{free base})}{(\text{salt})} = \frac{K}{k_b}.$$

The results for anthranilic acid hydrochloride were as follows, x being the amount hydrolysed:—

v.	x found.	x calculated for $k_b/K = 110$.
2	0·122	0·126
5	0·187	0·191
10	0·255	0·260
20	0·350	0·345
50	0·498	0·484

It will be seen that the dilution law does not hold strictly true, but the error introduced by calculation from one dilution to another is only a minor one, if the two dilutions be reasonably near one another.

Hydrion Concentration.—One of the most striking facts in connection with amphoteric electrolytes is that the conductivity does not give a direct estimate of the hydrion concentration.

Bredig and Fraenkel† have recently devised a simple method for the estimation of hydrion in small concentrations by the catalysis of diazo-acetic ester, the rate of the reaction, which is monomolecular, being followed by observing the amount of nitrogen evolved. The experiments with this method which are given in this paper were all performed in a thermostat at 25°. The same volumes were used in all cases to render the experiments comparable, namely 20 c.c. of the solution containing the hydrion, 0·1 c.c. of diazo-acetic ester, and 2 c.c. of ethyl-alcohol. The diazo-acetic ester was also weighed as a check. No reading was taken for the first few minutes after mixing.

* *Loc. cit.*

† *Loc. cit.*

Anthranilic Acid. $v = 32$.

t.	Reading.	x.	A$-x$.	c.
0	2·80	—	22·00	—
10	4·40	1·60	20·40	0·00328
20	5·83	3·03	18·97	321
42	8·50	5·70	16·30	310
82	12·93	10·13	11·87	327
141	17·40	14·60	7·40	336
232	21·15	18·35	3·65	336
∞	24·80	—	—	—
			Mean	0·00325

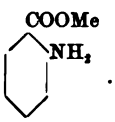
As a standard of comparison, acetic and benzoic acids were investigated under the same conditions.

N/64 benzoic acid, which has a hydrion concentration of $93{\cdot}7 \times 10^{-5}$, gave a constant of 0·0101 in the same units.

N/10 acetic acid with a hydrion concentration of 126×10^{-5} gave a constant of 0·0166.

The hydrion concentration of N/32 anthranilic acid, if the benzoic acid be taken as the standard of comparison, $= 30 \times 10^{-5}$, while if the acetic acid be used as the standard it is 25×10^{-5}.

Walker* has calculated the hydrion concentration in anthranilic acid solutions from the experimental data of Winkelblech, and according to his equations it should, in N/32 solution, be 27×10^{-5}, whilst a simple acid of similar conductivity would have a hydrion concentration of 47×10^{-5}. The result is thus in excellent accord with Walker's calculation.

Methyl Ester of Anthranilic Acid, 

For the determination of the strength of the ester as a base the twice crystallised hydrochloride was used. This was made from anthranilic acid,† and melted at 135°. Estimation of the chlorine resulted as follows:—

0·1880 gramme contained 0·0353 gramme of chlorine.

Found chlorine	18·75
Calculated for $C_8H_{10}O_2NCl$.....	18·90

* *Loc. cit.*

† Erdmann and Erdmann, 'Berichte,' vol. 32, p. 1215.

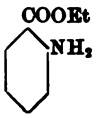
Methyl Acetate Catalysis.—0·3755 gramme of hydrochloride of methyl ester of anthranilic acid in 20 c.c. of water.

$v = 10$, A = 13·61.

t.	Titre.	*x.*	A−*x.*	*c.*
0	3·10	—	13·61	—
2770	7·93	4·83	8·78	0·000687
5490	11·00	7·90	5·71	687
7000	12·25	9·15	4·46	692
7600	12·77	9·67	3·94	707
8370	13·15	10·05	3·56	696
			Mean	0·000694

Comparison Solution.—N/10 for total chloride, N/40 for free HCl, $c = 0{\cdot}000749$, hydrolysis in N/10 solution = 23·2 per cent.

$k_b/K = 143$.

Ethyl Ester of Anthranilic Acid, 

The hydrochloride of this ester was prepared like the similar compounds and crystallised from alcohol. The melting point was 168°, and analysis of the amount of chlorine gave the following result:—

0·1735 gramme of the hydrochloride contained 0·0304 gramme of chlorine.

Chlorine found.....	17·50 per cent.
Calculated for $C_9H_{12}O_2NCl$.....	17·58 „

Methyl Acetate Catalysis.—The hydrochloride of this ester is so much hydrolysed in solution, and the ester itself so insoluble, that it was not found possible to work with a solution stronger than N/100, and the satisfactory estimate obtained at this dilution shows the wide applicability of the method.

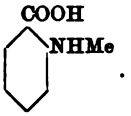
0·0410 gramme of the hydrochloride of the ethyl ester of anthranilic acid in 20 c.c. water.

$v = 100$. A = 27·10.

t.	Titre.	*x.*	A−*x.*	*c.*
0	0·23	—	27·10	—
370	2·50	2·27	24·83	0·0001027
625	3·85	3·62	23·48	0999
710	4·33	4·10	23·00	1004
870	5·16	4·93	22·17	1018
1110	6·40	6·17	20·93	1012
1385	7·75	7·52	19·58	1017
			Mean	0·0001013

Comparison Solution.—N/100 for chloride, N/200 for free hydrochloric acid, hydrolysis in N/100 solution = 57·8.

$$k_b/K = 126.$$

Monomethyl-anthranilic Acid, 

Two samples of this were prepared by different methods:—

(A) A quantitative yield was obtained by the use of methyl sulphate (Willstätter and Kahn). Reference has already been made to this method and an analysis given of the sample, which was crystallised from alcohol and then three times from water before use in the following experiments.

(B) Another sample, which was used only for a conductivity determination, was made by the action of methyl iodide and potash on anthranilic acid.* Before use the sample was crystallised six times from water.

Basic Constant.—Monomethyl-anthranilic acid is so insoluble that it was found necessary in the methyl acetate catalysis experiments to take more hydrochloric acid than corresponded to the amount of base, and to use supersaturated solutions, in order that the experiments might not be unduly prolonged.

As this diminishes the accuracy of the method, two experiments were performed with different ratios of acid to base.

Methyl Acetate Catalysis.—I. 0·1510 gramme of monomethyl-anthranilic acid in 50 c.c. of N/20 hydrochloric acid.

v for base = 50. v for acid = 20. A = 19·60.

t.	Titre.	x.	A − x.	c.
0	2·90	—	19·60	—
2965	12·30	9·40	10·20	0·0000957
3223	12·90	10·00	9·60	962
3790	14·03	11·13	8·47	962
4270	14·90	12·00	7·60	963
5360	16·50	13·60	6·00	959
6815	18·17	15·27	4·33	962
			Mean	0·0000961

Comparison Solution.—N/20 for total chloride, 0·036 N for free hydrochloric acid, mean c = 0·0000980.

$$k_b/K = 79·5.$$

* Schultz and Flachsländer, abstract in 'Chemisches Centralblatt,' (2), 448, 1902.

II. A solution was made from 0·1510 gramme monomethyl-anthranilic acid and 15 c.c. N/10 hydrochloric acid, diluted to 110 c.c. with water. These irregular quantities were taken because they were the smallest amounts of acid and water in which the base would remain dissolved, when the solution was cooled from the high temperature used to obtain the solution.

v for base = 110. v for acid = 73·3. A = 19·70.

t.	Titre.	x.	A−x.	c.
0	1·00	—	19·70	—
5,460	6·70	5·70	14·00	0·0000272
6,835	7·87	6·87	12·83	273
8,300	9·05	8·05	11·65	275
8,730	9·36	8·36	11·34	275
9,750	10·14	9·14	10·56	278
10,360	10·57	9·57	10·13	278
			Mean	0·0000275

Comparison Solution.—0·016 N for total chloride, N/100 for free hydrochloric acid, mean c = 0·0000290.

The method of calculation used to find k_b/K in an experiment such as the above is as follows:—

Base taken	0·00906 N	Free acid = $\frac{2}{2}\frac{7}{9}\frac{5}{0}$ × 0·1 ...	0·00948 N
Total acid taken	0·01364 N	Salt present	0·00416 N
		Free base present	0·00493 N

$$\frac{\text{Free acid} \times \text{free base}}{\text{salt}} = \frac{0{\cdot}00943 \times 0{\cdot}00493}{0{\cdot}00416} = 0{\cdot}0132 = \frac{K}{k_b}.$$

$$k_b/K = 75{\cdot}7.$$

Mean of I and II ..... $k_b/K = 77{\cdot}6$.

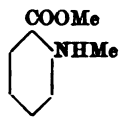
Acid Constant.—Monomethyl-anthranilic acid possesses marked acid properties, as was shown by the fact that it could be accurately titrated against soda with phenolphthalein as indicator. Its strength as an acid was found from the conductivity determinations, which were done on solutions prepared separately by dissolving weighed quantities of the acid in 1 litre of water in a bottle of "Resistenzglas."

Sample.	v.	μ.	100 m.	100 k.
A	775	21·1	5·74	0·000451
A	1025	24·9	6·62	0·000458
A	1510	31·1	8·16	0·000480
B	1510	30·4		

The conductivity of the sodium salt of monomethyl-anthranilic acid was also determined.

v	32	1024
μ	68·8	78·4

80 was taken as the value at infinite dilution, and this gave for monomethyl-anthranilic acid, $\mu_\infty = 376$. Turning to the acid constant to be deduced from these figures, examination of the tables given in Walker's paper show that where k_b is small, α and a are practically identical at high dilutions, such as were employed here. The value of k_a for monomethyl-anthranilic acid may be taken then as $0{\cdot}46 \times 10^{-5}$.

Methyl Ester of Monomethyl-anthranilic Acid, 

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Basic Constant.—The hydrochloride of monomethyl-anthranilic acid was prepared from the acid by the combined action of methyl alcohol and hydrogen chloride. It was a salt which crystallised from alcohol in fine, colourless needles, was very soluble in water, insoluble in ether, and melted at 218°.

The sample used was crystallised twice from alcohol and analysed for chlorine.

0·2010 gramme contained 0·0353 gramme of chlorine.

Chlorine found.....	17·56 per cent.
Calculated for $C_9H_{12}O_2NCl$.....	17·62 „

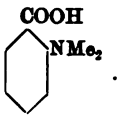
Methyl Acetate Catalysis.—0·8060 gramme of the hydrochloride of methyl ester of monomethyl-anthranilic acid was dissolved in 20 c.c. of water.

$v = 5$. A = 17·10.

t.	Titre.	x.	A−x.	c.
0	5·35	—	17·10	—
37·5	7·25	1·90	15·20	0·00137
85	9·35	4·00	13·10	139
135	11·37	6·02	11·08	140
160	12·20	6·85	19·25	139
183	12·95	7·60	9·50	140
280	15·60	10·25	6·85	142
351	17·00	11·65	5·45	141
			Mean	0·00140

Comparison Solution.—N/5 for chloride, N/100 for free hydrochloric acid mean $c = 0{\cdot}00170$.

$$k_b/K = 2780.$$

Dimethyl-anthranilic Acid, 

Basic Constant.—The method of preparation was that given by Willstätter and Kahn.* The acid was purified by three crystallisations from ether, and formed long, transparent needles which melted at 70°. Its strength as an acid was sufficient to prevent titration of acetic acid by phenolphthalein in its presence, but it was not strong enough to be titrated itself by the use of that indicator, so that it was found necessary to use *o*-nitrophenol as indicator in the catalysis experiment.

Methyl Acetate Catalysis.—0·3300 gramme of dimethyl-anthranilic acid in 20 c.c. of N/10 hydrochloric acid.

$v = 10.$ $A = 28{\cdot}05.$

t.	Titre.	*x.*	A−*x.*	*c.*
0	2·67	—	28·05	—
701	8·00	5·33	22·72	0·00131
942	9·65	6·98	21·07	132
1185	11·20	8·53	19·52	133
1365	12·25	9·58	18·47	133
2090	15·95	13·28	14·77	133
2380	17·20	14·53	13·52	133
2670	18·40	15·73	12·32	134
			Mean	0·00133

Comparison Solution.—N/10 for chloride, N/20 for free hydrochloric acid, mean $c = 0{\cdot}00141$, hydrolysis in N/10 solution = 47·2 per cent.

$$k_b/K = 23{\cdot}5.$$

Acid Constant.—Dimethyl-anthranilic acid crystallised so well from ether that an attempt was made to determine its strength as an acid by the conductivity, but with each recrystallisation the conductivity steadily diminished, until it was too near that of pure water to be of value. The last determination made with water of conductivity $1{\cdot}2 \times 10^{-6}$, in a cell with unplatinised electrodes, gave the following result.

v.	μ.	$100m$.	*k.*
8	0·0649	0·0172	$3{\cdot}8 \times 10^{-8}$

That the acid dissociation constant was not negligibly small was shown by the action on indicators, and also by the conductivity of the sodium salt, which exhibited evidence of but a small amount of hydrolysis.

* *Loc cit.*

Conductivity of sodium salt of dimethyl-anthranilic acid.

v	32·0	1024·0
μ	67·4	80·8

This experiment showed, however, that, though there was hydrolysis, it was very slight. The diazo-acetic ester method for the estimation of hydrion was also tried with a N/10 solution of dimethyl-anthranilic acid, but no measurable amount of nitrogen was evolved in two hours. This is a conclusive proof that the acid is extremely weak.

Methyl Acetate Saponification.—The methyl acetate saponification method of Shields did not adapt itself well to the case of dimethyl-anthranilic acid, since the only indicators with which one could estimate the acetic acid were more or less affected by the dimethyl acid. As the best available, *o*-nitrophenol was used, but it was not very satisfactory.

The solution was made by dissolving 0·258 gramme of dimethyl-anthranilic acid in 25 c.c. of N/16 sodium hydroxide and addition of 25 c.c. of N/16 methyl acetate solution.

$v = 32.$

t.	Titre.	x.	kc.
0	12·50	—	—
149	11·90	0·60	0·000066
222	10·63	1·87	60
400	10·40	2·10	45
1380	8·80	4·70	51
		Mean	0·000055

The saponification constant for soda and methyl acetate is 10·5, so that

$$\frac{k_a}{K} = \frac{10{\cdot}5}{0{\cdot}000055} = 1{\cdot}9 \times 10^5.$$

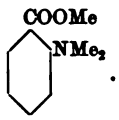
$$k_a = 1{\cdot}9 \times 10^5 \times 1{\cdot}2 \times 10^{-14} = 2{\cdot}3 \times 10^{-9}.$$

Physical Properties and Ring Formation.—It will be seen that there is a very marked drop in the acid dissociation constant when we introduce the second methyl group in the anthranilic series.

In the meta series, on the other hand, it was found that the mono- and di-methyl acids agreed closely in all their physical properties, such as solubility, appearance, and the acid and basic constants.

The following summary of the physical properties of dimethyl-anthranilic

acid, in comparison with the allied substances, leaves little doubt that the difference is stereochemical, and that this acid is more closely related to the betaines, possessing a tendency to ring formation, which would naturally be most marked in the ortho series. In the first place, dimethyl-anthranilic acid resembles in external appearance *o*-benzbetaine much more closely than it does anthranilic or monomethyl-anthranilic acid, since it forms soft, transparent crystals, which are characteristic of both ortho- and meta-benzbetaine. It dissolves also very readily in water and alcohol, and slightly in ether, thus agreeing with the betaines, but not with the other substances. The melting point of anthranilic acid is 144°; the mono derivative melts at 179°, whilst the dimethyl derivative melts at 70°. In the meta series the mono- and di-methyl derivatives melt within 4° of one another. The similarity to the betaine suggests ring formation in the molecule, and this would at once explain the low acid dissociation constant, since extensive ring formation and pronounced acid properties are incompatible.

Methyl Ester of Dimethyl-anthranilic Acid, 

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Basic Constant.—This ester was prepared by the method of Willstätter and Kahn, purified by distillation, and its strength as a base determined by a methyl acetate catalysis with the hydrochloride. The hydrochloride was prepared by passing hydrogen chloride through an ethereal solution of the ester, when the salt separated as a white crystalline solid, which was purified by several washings with ether.

The hydrochloride of the methyl ester of dimethyl-anthranilic acid, which has not been previously described, melts with decomposition at 145° to 147°, is very soluble in water, soluble in alcohol, insoluble in ether, and is slightly deliquescent. Its identity was confirmed by analysis of the amount of chlorine.

0·1925 gramme of the hydrochloride contained 0·0297 gramme of the chlorine.

Chlorine found	16·40 per cent.
Calculated for $C_{10}H_{14}O_2NCl$	16·45 „

Methyl Acetate Catalysis.—0·862 gramme of the hydrochloride of the methyl ester of dimethyl-anthranilic acid was dissolved in 20 c.c. of water.

$v = 5$. A = 28·18.

t.	Titre.	x.	A−x.	c.
0	5·30	—	28·18	—
89·5	11·37	6·07	22·11	0·000118
114	13·30	8·00	20·18	128
118	13·60	8·30	19·88	128
138	16·75	11·45	16·73	140
143	17·15	11·85	16·33	142
			Mean	0·000131

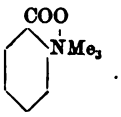
Comparison Solution.—N/5 for chloride, N/200 for free hydrochloric acid, mean $c = 0{\cdot}0000880$.

$$k_b/\mathrm{K} = 3500.$$

It will be seen that c is here only approximately a constant, as it showed a steady increase with time. It was found by repetition of the experiment that this was a real variation and not due to experimental error. In another set of experiments, in which the readings were taken at an earlier stage of the reaction, the value obtained for k_b/K was somewhat higher, viz., 4200. The explanation is, doubtless, that the methyl ester of dimethyl-anthranilic acid undergoes slight hydrolysis (saponification) itself during the course of the reaction, and the hydrolysis of any of this ester involves the liberation of an equivalent quantity of hydrochloric acid, since at such a great dilution any hydrochloride of dimethyl-anthranilic acid would be almost completely hydrolysed. The influence of such a secondary action would be very small if the ester hydrochloride were much hydrolysed, but when we are dealing with a comparatively strong base, such as we have here, the effect on the apparent k_b/K is at its maximum.

As an instance, we may consider an ester whose real k_b/K is 7800, and suppose that in N/5 solution the ester is itself hydrolysed 1 per cent. before the readings are taken; the apparent k_b/K will then be 3100.

The k_b/K for the methyl ester of dimethyl-anthranilic acid may, therefore, be taken as not below 4000, and from a consideration of the rate at which the constant falls off with time, it is probable that the real k_b/K lies between 5000 and 6000.

o-Benzbetaine, 

Basic Constant.—*o*-benzbetaine, prepared by the method of Willstätter and Kahn, was repeatedly crystallised from alcohol, and in this manner obtained in large transparent crystals, which melted at 225°. The basic dissociation

constant was found by a methyl acetate catalysis with a solution of the hydrochloride prepared from the pure betaine and an equivalent quantity of hydrochloric acid.

Methyl Acetate Catalysis.—0·3760 gramme of *o*-benzbetaine in 20 c.c. of N/10 hydrochloric acid.

$v = 10.$ $A = 17·00.$

t.	Titre.	*x.*	A−*x.*	*c.*
0	2·60	—	17·00	—
488	4·95	2·35	14·65	0·000132
790	6·30	3·70	13·30	135
1430	8·57	5·97	11·03	132
1799	9·90	7·30	9·70	135
2020	10·48	7·88	9·12	134
2160	10·95	8·35	8·65	135
2990	12·80	10·20	6·80	133
			Mean	0·000134

Comparison Solution.—N/10 for chlorides, 0·07 N for free hydrochloric acid, mean $c = 0·000199$, hydrolysis of *o*-benzbetaine hydrochloride in N/10 solution = 47 per cent.

$$k_b/K = 23·2.$$

Acid Constant.—*o*-benzbetaine, which had been several times crystallised from alcohol, was found to possess an appreciable conductivity, but further careful crystallisation produced a steady lowering, until the last conductivity obtained from a N/16 solution was only three times that of pure water.

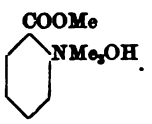
The method of Shields was therefore used, and, as a preliminary experiment showed the hydrolysis to be very large, a solution of pure caustic soda was employed as a comparison:—

(A) 0·295 gramme of *o*-benzbetaine was dissolved in 25 c.c. of N/16 sodium hydroxide and diluted to 100 c.c. This was mixed with 100 c.c. of of N/64 methyl acetate, so that the final dilution of all constituents was 128.

(B) 100 c.c. N/64 sodium hydroxide solution was mixed with 100 c.c. of N/64 methyl acetate, and v was here also 128.

t.	Pure NaOH.	NaOH with *o*-benzbetaine.
0	15·50	15·50
8	8·85	—
11	—	7·55
20	5·25	5·20
37	3·35	3·35

It is evident that all the caustic soda is free, and the conclusion is, therefore, that *o*-benzbetaine possesses no measurable acid properties.

The Hydroxide of the Methyl Ester of o-Benzbetaine, 

Willstätter and Kahn have shown that if an aqueous solution of the methiodide of the methyl ester of dimethyl-anthranilic acid is acted on by silver oxide at zero, a strong base is obtained, which quickly disappears, and the solution is found to contain only the *o*-benzbetaine. The base is undoubtedly the hydroxide of the methyl ester of *o*-benzbetaine, and the methiodide the iodide of the same base. This iodide is quite stable in aqueous solution and it was, therefore, prepared and purified by two crystallisations from water. It melted at 153°, and analysis for iodine gave the following result:—

0·3165 gramme of the iodide contained 0·1234 gramme of iodine.

Iodine found.....	39·0	per cent.
Calculated for $C_{11}H_{16}O_2NI$	39·46	„

Basic Strength of the Hydroxide.—An attempt was made to find the extent of hydrolysis of the iodide in N/5 solution by catalysis of methyl acetate, but it was too small to detect in this manner.

By the delicate method of Bredig and Fraenkel extremely minute concentrations of hydrion can be readily recognised, but a N/50 solution of the iodide of the methyl ester of *o*-benzbetaine, when mixed with diazo-acetic ester in the usual manner, caused no evolution of nitrogen at all. This proved conclusively that there was no appreciable hydrolysis.

Autosaponification of the Hydroxide of the Methyl Ester of o-Benzbetaine.—An ice-cold solution of the methiodide of *o*-benzbetaine,

$$C_6H_4.N(CH_3)_3I.COOCH_3,$$

was mixed with a measured volume of ice-cold water in which excess of freshly prepared and thoroughly washed silver oxide was suspended.

After shaking for two or three minutes, the solution was filtered off from the silver oxide and iodide. If the temperature was kept very near zero throughout, an almost quantitative yield of the tetramethyl derivative was obtained, provided that the solutions were very dilute.

The hydroxide of the methyl ester of *o*-benzbetaine is a substance of peculiar interest, since it is at the same time a strong base and an ester. The experiments with its iodide showed the base to be a very strong one, and it was found that even in very dilute solution it quickly decomposed. Since the end products were neutral, this reaction could be readily followed by

titration, and it was conclusively proved that the decomposition was due to the saponification of the ester part of the molecule by the hydroxidion which the same substance formed in virtue of its property as a base.

Rate of Decomposition.—100 c.c. of N/50 tetramethyl iodide solution was shaken with 100 c.c. of water containing excess of silver oxide, and immediately filtered. Precautions were taken to keep the temperature as near 0° as possible, and the solution after filtration was kept in a vessel surrounded by finely crushed ice. The solution was found by the first titration to be 0·00995 N.

t.	Titre.	*x.*	*c.*	*k.*
0	9·95	—	—	—
14	9·50	0·45	0·00159	0·329
31	8·95	1·00	0·00156	0·278
103	7·50	2·45	0·00121	0·317
163	6·82	3·13	0·00102	0·282
273	5·26	4·69	0·00086	0·321
			Mean	0·31

c should be a constant if the action were monomolecular, whilst if we take the action as bimolecular we should get

$$k = \frac{1}{At} \cdot \frac{x}{(A-x)},$$

where A is the total change expressed in terms of a normal solution, and x is the amount changed in any time t.

The reaction is evidently bimolecular, as it should be if it were an action between an ester and the hydroxidion produced by the electrolytic dissociation of the basic group.

Rate of Decomposition in Presence of Sodium Hydroxide.—To obtain a comparison between the strength of the base and that of sodium hydroxide, a similar experiment was performed under identical conditions, except that the solution was made not only N/100 for the ester-base, but also N/100 for sodium hydroxide.

t.	Titre.	*x.*	*k.*
0	19·65	—	—
10	18·92	0·73	0·848
42	17·40	2·25	0·744
104	15·45	4·20	0·768
145	14·40	5·25	0·853
177	13·80	5·85	0·902
		Mean	0·82

The constant k is calculated as before from the equation—

$$k = \frac{1}{At} \cdot \frac{x}{A-x}.$$

From this it appears that the rate at which the ester-base saponified itself is roughly half that at which the saponification occurred when an equivalent amount of sodium hydroxide was also present. Strictly the above equation should have been replaced by one taking account of the two reactions.

$$\frac{d(x+y)}{dt} = k_1(A-x)^2 + k_2(A-y)(A-x),$$

where A is the original concentration of the ester-base and also of the sodium hydroxide, and x and y the amounts hydrolysed by the ester-base and the sodium hydroxide respectively in any time t. The data are not sufficiently accurate to test this equation, but the evidence supports the assumption that x and y are approximately equal, *i.e.*, that the ester-base supplies as much hydroxidion as the sodium hydroxide.

Rate of Decomposition in Presence of Methyl Acetate.—Perhaps the most convincing proof that the hydroxide of the methyl ester of *o*-benzbetaine is really a strong base, and yields hydroxidion, was afforded by its action on methyl acetate. A solution of the ester-base was prepared from the iodide with silver oxide, and sufficient methyl acetate solution added to make the mixed solution 0·01 N for both constituents. The solution was at once filtered, and titrated at intervals, being kept at zero as in the previous experiments.

t.	Titre.	x.
0	8·30	—
10	6·63	1·67
20	5·78	2·52
36	4·65	3·65
71	3·20	5·10
97	2·55	5·75
1100	0·10	8·20

The equilibrium in the above solution is so complex that no attempt has been made to calculate the constant for the reaction, but a comparison of these figures with those given for the auto-saponification of the ester-base at the same temperature and dilution show that the methyl acetate was rapidly saponified by the ester-base, which thus possesses basic properties comparable with those of sodium hydroxide.

Conductivity of the Hydroxide of the Methyl Ester of o-Benzbetaine.—The conductivity of the tetramethyl derivative in comparison with that of

sodium hydroxide is of some interest. The constant of the cell was determined at 1°, and measurements were then made at about that temperature with N/60 sodium hydroxide and N/60 hydroxide of the methyl ester of *o*-benzbetaine, under conditions as nearly identical as possible. The N/60 hydroxide of the methyl ester of *o*-benzbetaine was prepared from its iodide by interaction with thoroughly washed silver hydroxide, and filtered at once into the measuring vessel. From the amount of iodide used and the volume, the strength of the solution should have been 0·0167 N. From a titration made immediately after the filtration, it was found to be 0·0163 N.

Conductivity of the Hydroxide of the Methyl Ester of *o*-Benzbetaine.

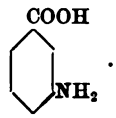
Time after filling vessel.	Temp.	*v*.	λ.
3	1°·2	60	0·134
8	0·7	60	0·123

Conductivity of Sodium Hydroxide under the same Conditions.

Time after filling vessel.	Temp.	*v*.	λ.
10	1°·1	60	0·147
15	0·8	60	0·133

The agreement is sufficiently close to show that the dissociation and ionic velocities must be of the same order of magnitude.

It may be remarked that it would be possible to follow the self-saponification of the ester-base by means of the conductivity, since the ester-base is a strong electrolyte, while the products *o*-benzbetaine and methyl alcohol are non-electrolytes. In the above experiment the conductivity fell about 1/6 in one hour.

m-Aminobenzoic Acid, 

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Hydrion Concentration.—The diazo-acetic ester method for the estimation of hydrion was tried at various dilutions.

The constants for acetic and benzoic acids have already been given under anthranilic acid. If benzoic acid be taken as the standard, the hydrion concentration in N/64 *m*-aminobenzoic acid is 28×10^{-5}. With acetic acid as standard it is 22×10^{-5}. Walker's calculated value is $11{\cdot}8 \times 10^{-5}$, while that of a simple acid with a conductivity equal to that of *m*-aminobenzoic acid would be $40{\cdot}8 \times 10^{-5}$.

$v = 64$.

t.	Reading.	*x.*	A−*x.*	*c.*
0	1·75	—	22·20	—
33	6·28	4·53	17·67	0·00301
44	7·60	5·85	16·35	293
62	9·55	7·80	14·40	303
91	12·10	10·35	11·85	299
123	14·37	12·62	9·50	300
182	15·13	13·38	8·82	304
			Mean	0·00300

$v = 64$.

t.	Reading.	*x.*	A−*x.*	*c.*
0	1·60	—	22·40	—
35	6·70	5·10	17·30	0·00320
40	7·25	5·65	16·75	315
50	8·50	6·90	15·50	320
60	9·55	7·95	14·45	317
80	11·37	9·77	12·63	311
90	12·32	10·72	11·68	314
100	13·18	11·58	10·82	316
			Mean	0·00316

$v = 256$.

t.	Reading.	*x.*	A−*x.*	*c.*
0	2·70	—	22·40	—
30	6·08	3·38	19·02	0·00236
40	7·00	4·30	18·10	231
50	8·00	5·30	17·10	232
63	9·07	6·37	16·03	231
84	10·78	8·08	14·32	231
103	12·10	9·40	13·00	230
			Mean	0·00232

$v = 512$.

t.	Reading.	x.	A$-x$.	c.
0	1·50	—	24·50	—
33	5·50	4·00	20·50	0·00235
46	7·15	5·65	18·85	247
61	8·70	7·20	17·30	242
87	10·57	9·07	15·43	236
110	12·50	11·00	13·50	235
121	13·23	11·73	12·87	231
			Mean	0·00238

$v = 1024$.

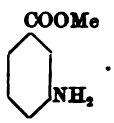
t.	Reading.	x.	A$-x$.	c.
0	3·20	—	22·40	—
70	8·70	5·50	16·90	0·00174
107	10·95	7·75	14·65	173
140	12·90	9·70	12·70	176
176	14·57	11·37	11·03	175
203	15·70	12·50	9·90	175
269	17·83	14·63	7·77	171
			Mean	0·00174

There are several causes which may contribute to the discrepancy between the calculated and the observed value, for instance, the influence of ionised salt on the diazo-acetic ester. According to Walker's theory there must be ionised salt present, since *m*-aminobenzoic acid possesses marked acid and basic properties. Further, we have no positive knowledge of the effect of unionised molecules, or of the addition of alcohol to an aqueous solution of an amphoteric electrolyte.

There is, however, a method of comparison which is open to less uncertainty, namely, to ascertain the effect of dilution on the hydrion concentration. In this case the influence of disturbing factors should be regular throughout.

It was found by experiment that the hydrion concentration of N/64 benzoic acid was roughly double that of a N/256 solution, as should be the case with a simple acid, according to Ostwald's dilution law. The divergence of an amphoteric electrolyte from the simple law is clearly shown in the following table, in which the hydrion concentration with $v = 64$ has been called 100, the figures for the other dilutions being calculated on this basis:—

v	64.	128.	256.	512.	1024.
Experimental for *m*-aminobenzoic acid	100	—	75·3	77·1	56·5
Calculated from Walker's paper	100	96·7	91·0	82·2	69·8
Calculated for a simple acid	100	71	50	35	25

Methyl Ester of m-Aminobenzoic Acid, 

Basic Constant.—The strength of this ester as a base was found by a methyl acetate catalysis with the hydrochloride, the preparation of which has already been described.

Methyl Acetate Catalysis.—1·870 grammes of the hydrochloride of the methyl ester of *m*-aminobenzoic acid were dissolved in 20 c.c. of water.

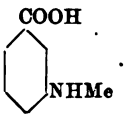
$v = 2.$ $A = 16{\cdot}20.$

t.	Titre.	x.	$A-x$.	c.
0	13·70	—	16·20	—
370	16·65	2·95	13·25	0·000236
583	18·13	4·43	11·77	237
1070	20·88	7·18	9·02	237
1320	21·95	8·25	7·95	234
1550	22·93	9·23	6·97	236
			Mean	0·000236

Comparison Solutions.—(1) N/2 for chloride, N/100 for free hydrochloric acid; mean $c = 0{\cdot}000202$.

(2) N/2 for chloride, N/66·7 for free hydrochloric acid; mean $c = 0{\cdot}000306$.

$k_b/K = 3600.$

Monomethyl m-Aminobenzoic Acid, 

Basic Constant.—Whenever possible it is preferable to use a crystalline salt in making up a solution for hydrolysis purposes and, accordingly, a methyl acetate catalysis was performed with the thrice crystallised hydriodide of monomethyl *m*-aminobenzoic acid, the preparation and analysis of which will be found in the first part of this paper.

Methyl Acetate Catalysis.—0·585 gramme of the hydriodide of monomethyl *m*-aminobenzoic acid in 20 c.c. of water. $v = 10$.

t.	Titre.	x.	A$-x$.	c.
0	3·97	—	12·85	—
1103	7·30	3·33	9·52	0·000119
1350	7·97	4·00	8·85	120
1435	8·16	4·19	8·66	119
1593	8·50	4·53	8·32	119
1680	8·73	4·76	8·09	120
			Mean	0·000119

Comparison Solution.—N/10 for chloride, N/200 for free hydrochloric acid, mean $c = 0{\cdot}000843$, hydrolysis in N/10 solution = 7·1 per cent.

$$k_b/\mathrm{K} = 1580.$$

These results appeared to fix the basic strength of monomethyl *m*-aminobenzoic acid with fair certainty, but when it was found that an iodide is liable to give too high a result, the chloride was tried.

It was not found possible to obtain the chloride in a pure crystalline state, so hydrochloric acid was added to weighed quantities of monomethyl *m*-aminobenzoic acid. The first two experiments gave the hydrolysis in N/10 solution as 16 per cent. and 15·2 per cent. respectively, which would mean that the k_b/K was about 350, as against 1850 from the experiment with the iodide. There seemed a possibility that the acid had oxidised in the chloride experiments, and an experiment was therefore performed in a flask from which the air was expelled after each titration with nitrogen. The result was as follows:—

Methyl Acetate Catalysis.—0·302 gramme of monomethyl *m*-aminobenzoic acid in 20 c.c. of N/10 hydrochloric acid. $v = 10$.

t.	Titre.	x.	A$-x$.	c.
0	4·70	—	25·20	—
452	9·18	4·48	20·72	0·000184
677	10·98	6·28	18·92	183
740	11·50	6·80	18·40	185
931	13·00	8·30	16·90	186
			Mean	0·000184

Comparison Solution.—N/10 for chloride, N/100 for free hydrochloric acid, mean $c = 0{\cdot}000182$, hydrolysis in N/10 solution = 10·1 per cent.

$$k_b/\mathrm{K} = 900.$$

The difference between the values obtained from the chloride and iodide is still large, and there seems no means of determining the exact value. As that from the chloride is probably too low, and the iodide value too high, k_b/K has been taken as 1000 in the calculation of the acid constant from the conductivity.

Conductivity and Acid Constant.—Though monomethyl *m*-aminobenzoic acid was repeatedly crystallised, it was not found possible to obtain it quite free from colour, but the sample used for the conductivity was almost colourless.

Conductivity of the Sodium Salt.—

$v = 32$, $\mu = 69{\cdot}9$. $v = 1024$, $\mu = 79{\cdot}7$.

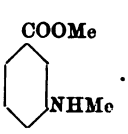
μ_∞ was taken as 81, and μ_∞ for the monomethyl *m*-aminobenzoic acid as 377.

$\mu'_\infty = 66$, so that $\alpha = a + 66/377d$.

Conductivity of Monomethyl m-Aminobenzoic Acid.—The water used had a conductivity of $0{\cdot}9 \times 10^{-6}$. The solutions were made in glass vessels, which were known not to alter the conductivity. $k_b/K = 1000$.

v.	μ experiment.	μ calculated for $k_a = 0{\cdot}8 \times 10^{-5}$.	$k_0 \times 10^{-5}$ experiment.	k_0 calculated for $k_a = 0{\cdot}8 \times 10^{-5}$.
82	7·47	7·51	0·488	0·493
164	9·90	9·66	0·430	0·411
328	14·0	13·6	0·436	0·414
656	21·1	20·3	0·506	0·467
1312	32·1	31·7	0·665	0·575
1312	31·6		0·586	

In view of the uncertainty as to the exact value of k_b/K, the agreement between the experimental and calculated values of the molecular conductivity μ may be regarded as satisfactory.

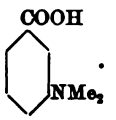
Methyl Ester of Monomethyl m-Aminobenzoic Acid, 

Although both the ester and its hydrochloride were prepared, no value can be given for the basic constant of this ester on account of its extreme insolubility. On addition of water to the hydrochloride, the hydrochloric acid all dissolves, but none of the ester.

The Löwenherz solubility method was tried, but a litre of N/2 hydrochloric acid only dissolved a few milligrammes of the ester. Farmer's*

* Farmer and Warth, 'Chem. Soc. Journ.,' vol. 85, p. 1713, 1904.

method was also tried, using benzene as the non-aqueous solvent, but the whole of the ester dissolved in the benzene and none in the water.

Dimethyl m-Aminobenzoic Acid, 

Basic Constant.—The specimen used for the physical determinations was prepared from *m*-benzbetaine,* and crystallised once from alcohol and twice from water. The strength as a base was found by catalysis of methyl acetate.

Methyl Acetate Catalysis.—0·1650 gramme of dimethyl *m*-aminobenzoic acid was dissolved in 10 c.c. of N/10 hydrochloric acid, and 5 c.c. of water. $v = 15$, $A = 15{\cdot}75$.

t.	Titre.	x.	$A-x$.	c.
0	2·68	—	15·75	—
508	4·45	1·77	13·98	0·0000102
743	5·28	2·60	13·15	106
1870	8·57	5·89	9·86	109
2350	9·70	7·02	8·73	109
			Mean	0·0000106

Comparison Solution.—N/15 for chloride, N/150 for free hydrochloric acid, $c = 0{\cdot}0000115$.

$$k_b/K = 1630.$$

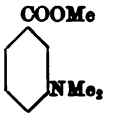
A repetition of this determination with a sample of dimethyl acid prepared by the new method gave $k_b/K = 1580$, the experiment being performed in N/10 solution in the same manner as the above.

Acid Constant.—The preparation of this substance has already been described. The sample used was several times crystallised from water. The conductivity of the sodium salt at $v = 1024$ was 77·5, and the figures used for μ_∞ and μ'_∞ were, therefore, $(79+296) = 375$, and $(375-347)\times 2+6 = 62$ respectively. The value of k_b/K used in the calculations was 1580. The water used had a conductivity of $1{\cdot}2\times 10^{-6}$.

v.	μ experiment.	k_0 experiment.	k_0 calculated for $k_a = 0{\cdot}8\times 10^{-5}$.
128	8·55	0·415	0·43
256	11·9	0·405	0·40
512	17·4	0·44	0·39
1024	26·9	0·54	0·45
1024	27·0	0·55	0·45

* Griess, *loc. cit.*

The reason for the discrepancy in this case between the theoretical and experimental numbers is not apparent. It is probably connected with the high value of k_b/K.

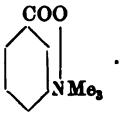
Methyl Ester of Dimethyl m-Aminobenzoic Acid, 

Methyl Acetate Catalysis.—0·864 gramme of the hydrochloride of the methyl ester of dimethyl *m*-aminobenzoic acid was dissolved in 25 c.c. of water. $v = 6{\cdot}25$, $A = 22{\cdot}50$.

t.	Titre.	*x.*	A − *x.*	*c.*
0	4·00	—	22·50	—
76	7·35	3·35	19·15	0·00092
119	9·06	5·06	17·44	93
168	10·92	6·92	15·58	95
190	11·82	7·82	14·68	97
			Mean	0·00094

Comparison Solution.—N/6 for chloride, 0·006 N for free hydrochloric acid, $c = 0{\cdot}000111$; the constants were 0·000110, 111, 112, 112.

$$k_b/K = 6000.$$

m-Benzbetaine, 

Basic Constant.—*m*-Benzbetaine is deliquescent and the hydrochloride was therefore prepared for the methyl acetate catalysis, which was performed also with the hydriodide.

Methyl Acetate Catalysis.—0·861 gramme of the hydrochloride of *m*-benzbetaine in 20 c.c. of water. $v = 5$, $A = 16{\cdot}20$.

t.	Titre.	*x.*	A − *x.*	*c.*
0	2·65	—	16·20	—
71·5	6·20	3·55	12·65	0·00151
76·2	6·51	3·86	12·34	155
92·5	7·25	4·60	11·60	157
97·0	7·40	4·75	11·45	155
139	9·14	6·49	9·71	160
			Mean	0·00156

Comparison Solution.—N/5 for chlorides, N/100 for free hydrochloric acid, mean $c = 0{\cdot}00188$, hydrolysis of betaine hydrochloride in N/5 solution = 4·14 per cent.

$$k_b/K = 2800.$$

A similar experiment with *m*-benzbetaine hydriodide showed it to be 3·96 per cent. hydrolysed, or with a k_b/K of 3060. Probably the lower value is the more correct, as it has already been mentioned that iodides show less than the true amount of hydrolysis.

Acid Constant.—*m*-Benzbetaine crystallised from alcohol, but on account of its great solubility and deliquescence it was not found possible to reduce the conductivity to a minimum, as it continued to fall with each recrystallisation.

Saponification of methyl acetate, in the same manner as described under *o*-benzbetaine, was performed with three solutions which were all N/128 for sodium hydroxide, but contained respectively no betaine, one equivalent of betaine, and two equivalents of the betaine. The results are given in this table:—

t.	Pure NaOH N/128.	N/128 NaOH and N/128 *m*-benzbetaine.	N/128 NaOH and N/64 *m*-benzbetaine.
0	15·50	15·50	15·50
8	8·85	8·70	8·20
15	6·35	6·35	6·30
20	5·25	5·40	5·05

It is evident that *m*-benzbetaine, like the similar ortho compound, is practically devoid of acid properties.

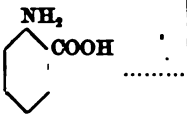
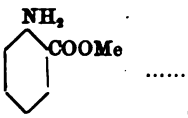
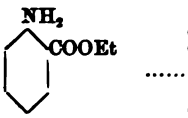
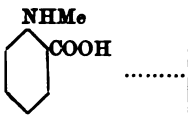
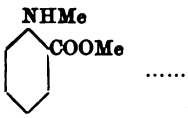
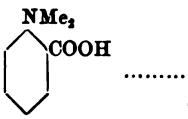
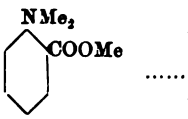
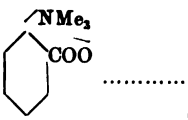
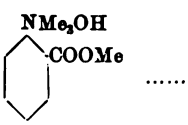
The Hydroxide of the Methyl Ester of m-Benzbetaine.

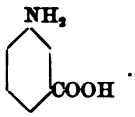
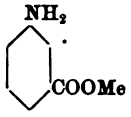
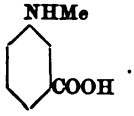
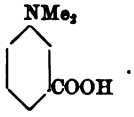
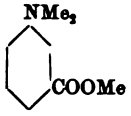
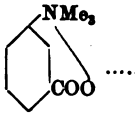
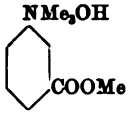
Basic Strength.—The iodide of this base was faintly acid to azolitmin, but neutral to other indicators. No hydrolysis could, however, be detected in N/64 solution with diazo-acetic ether, and the base was evidently very strong.

Addition of moist silver oxide to a cold solution of the iodide gave a strongly alkaline solution which became neutral in a few minutes.

This hydroxide, like the corresponding ortho compound, has a basic constant of the same order of magnitude as caustic soda.

Summary of Results.

	k_a.	k_a/K.	k_b.	k_b/K.
	$1 \cdot 04 \times 10^{-5}$	$8 \cdot 6 \times 10^{8}$	$1 \cdot 3 \times 10^{-12}$	110
	—	—	$1 \cdot 7 \times 10^{-12}$	143
	—	—	$1 \cdot 5 \times 10^{-12}$	126
	$0 \cdot 46 \times 10^{-5}$	$3 \cdot 8 \times 10^{8}$	$0 \cdot 94 \times 10^{-12}$	77
	—	—	$33 \cdot 6 \times 10^{-12}$	2780
	$0 \cdot 00023 \times 10^{-5}$	$1 \cdot 9 \times 10^{3}$	$0 \cdot 28 \times 10^{-12}$	23 ·5
	—	—	$60 \cdot 5 \times 10^{-12}$	5000
	$< 10^{-11}$	< 1	$0 \cdot 28 \times 10^{-12}$	23 ·2
	—	—	Very great	Very great

	k_a.	k_a/K.	k_b.	k_b/K.
	$1 \cdot 63 \times 10^{-5}$	$13 \cdot 5 \times 10^{8}$	$13 \cdot 3 \times 10^{-12}$	1110
	—	—	$43 \cdot 6 \times 10^{-12}$	3600
	$0 \cdot 8 \times 10^{-5}$	$6 \cdot 6 \times 10^{8}$	*ca.* 12×10^{-12}	*ca.* 1000
	$0 \cdot 8 \times 10^{-5}$	$6 \cdot 6 \times 10^{8}$	$19 \cdot 4 \times 10^{-12}$	1600
	—	—	73×10^{-12}	6000
	$< 10^{-14}$	< 1	34×10^{-12}	2800
	—	—	Very great	Very great

The Affinity Constants of Amphoteric Electrolytes. III. Methylated Amino-acids.

By Percival Jocelyn Wallace, B.Sc.

(Received May 21, Read May 31, 1928.)

(From the Chemical Laboratory, University College, Dundee.)

The main object of the present communication is to discuss the results obtained by Johnston and Cumming* in their investigation of the affinity constants of methylated amino acids. Before entering on the discussion of these amphoteric electrolytes, however, it is necessary to refer to certain general principles applicable to the affinity constants of simple electrolytes, in particular of simple bases.

Amino bases and their alkyl derivatives are supposed to exist in aqueous solution to a greater or less degree in the hydrated form, and it is this hydrated form which we conceive to give rise to the characteristic ion OH′ of soluble bases. Thus the alkalinity of ammonia solution is attributed primarily to the formation of ammonium hydroxide, according to the equilibrium equations

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH'.$$

Now, when we calculate the dissociation constant k_b of such a base from measurements of conductivity, catalysis, or salt hydrolysis, the constant obtained is not the constant for the equilibrium between the non-ionised hydroxide and its ions but one which is a function of this ionisation constant and of the hydration constant in addition.† Thus a stoichiometrical comparison of the values of k_b for such bases is not so simple as the corresponding comparison of k_a for acids, since in general for acids no effective hydration is involved. The value of the constant is, then, depends not only on the direct effect of a substituent on the ionisation equilibrium, but also on the effect of the same substituent on the hydration equilibrium.

It is of course reasonable to expect that a substituent which increases the dissociation constant of an acid will decrease to some degree that of a base, and we shall see that we are to be in general the case in the comparison of the acids and bases considered given in the subjoined table —

* See succeeding paper, p. 78.

† Compare Walker, Chem. Soc. Journ., 1894, 65, 486.

	X = COOH $k_a \times 10^5$.	X = NH_3OH or $NH_2 + H_2O$ $k_b \times 10^5$.
H.X	21·4	2·3
HO.X	*0·03*	—
CH_3.X	1·8	52
CH_2Me.X	1·34	56
$CHMe_2$.X	1·44	53
CMe_3.X	0·98	32
$C_6H_5.CH_2$.X	5·6	2·4
C_6H_5.X	6·0	*0·00005*

On the one hand we have the group of acetic acid and its methyl derivatives, on the other the group of methylamine and its *C*-methyl derivatives; in each of these groups the constants vary but little. Compared with formic acid and phenylacetic acid, the constants of the first group are considerably smaller; compared with the corresponding bases, ammonia and benzylamine, the constants of the second group are considerably greater. As no change in the hydration takes place in the acids considered, we may take it, from the general regularity displayed, that no change, or at least no great change, takes place in the hydration of the corresponding bases.

Consider, now, carbonic acid, HO.COOH, the second member in the list of acids given above. Generally speaking, the substitution of hydroxyl for hydrogen in the case of fatty acids effects a marked increase in the value of the acid constant. The degree of hydration remaining the same, we should therefore expect that the acid constant of carbonic acid, HO.COOH, should be decidedly greater than that of formic acid, H.COOH, of which it is the hydroxyl derivative. We find, instead, that it has only 1/700 of the value of the constant for formic acid. The conclusion may therefore be drawn that in the aqueous solution of carbonic acid by far the greater portion of the dissolved substance exists as the anhydride CO_2.

Similar reasoning may be applied to the bases. From the fact that the acid constants of benzoic acid, $C_6H_5.COOH$, and of phenylacetic acid, $C_6H_5.CH_2.COOH$, are nearly equal, we conclude that the carboxyl group may be attached directly to the benzene nucleus, or indirectly through the group CH_2 without any decided change in the ionisation of the resulting acid taking place. It is, therefore, probable that little change in the ionisation proper will result from the direct or indirect nature of the attachment of the basic group NH_2 (or NH_3OH) to the benzene nucleus, *i.e.*, we might expect aniline, $C_6H_5.NH_2$, and benzylamine, $C_6H_5.CH_2.NH_2$ to have nearly equal basic constants, the former perhaps slightly lower

Instead of this relation we find that the basic constant of aniline is only 1/50000 part of that of benzylamine. We consequently attribute the smallness of the basic constant of aniline, and other derivatives in which the basic group is attached directly to the benzene nucleus, to a great diminution in the degree of hydration as compared with that of the bases in which the basic group is not in direct union with the benzene nucleus. That the great diminution of the constant in the former case is not directly due to the influence of the phenyl group is sufficiently attested by the powerfully basic character of the compound $C_6H_5.NMe_3OH$. Here the formation of an anhydride is impossible, and although the basic group is directly united to the benzene nucleus, the base is as powerful as those in which the union is indirect. Since the alkyl derivatives of aniline have values of k_b of the same order as aniline itself, it seems not unsafe to deduce that all these substances as a group have approximately the same degree of hydration.

The bases considered above are all primary. Bredig* has shown that secondary bases have greater constants than the corresponding primary bases, when the substituting groups are alkyls, but that, contrary to expectation, the tertiary bases are considerably weaker than the secondary bases, being roughly of the same order of strength as the primary bases to which they correspond. Here, again, we probably have, owing to stereochemical influence, diminution in the hydration of the tertiary bases. The nature of the variation may be illustrated from ammonia and its methyl derivatives :—

	$k_b \times 10^5$.
Ammonia, NH_3	2·3
Methylamine, NH_2Me.....	50
Dimethylamine, $NHMe_2$.....	74
Trimethylamine, NMe_3	7·4

In the quaternary bases the hydration is necessarily complete, and the basic constant is incomparably greater, tetramethylammonium hydroxide, NMe_4OH, being as strong a base as caustic potash.

When we consider the effect of a substituent in an amphoteric electrolyte, the question becomes still more complicated, because we have to deal with it from the point of view of acid as well as of base, and because there is, in addition to the possibility of dehydration of the basic group in the ordinary sense, the possibility of ring-formation† which affects both acidic and basic

* 'Zeit. physikal. Chem.,' vol. 13, p. 299, 1894.

† Compare Sakurai, 'Chem. Soc. Proc.,' p. 90, 1894 ; p. 38, 1896.

constants.* Thus the amphoteric amino-acid, generally written $R<^{NH_2}_{COOH}$, may exist in the non-ionised state in the solution as $R<^{NH_2}_{COOH}$, $R<^{NH_3OH}_{COOH}$, and $R<^{NH_3}_{COO}$, without our being able to distinguish directly between these various forms. The further complication of a "hermaphrodite ion" (*Zwitterion*), $R<^{NH_3^+}_{COO^-}$, need scarcely be considered, as in the present state of our knowledge concerning amphoteric electrolytes its assumption is unnecessary to explain the known phenomena.

In discussing the constants of amphoteric electrolytes, therefore, we must bear in mind that ring-formation will diminish the value of both acidic and basic constants, and prepare to encounter this disturbing factor in the comparison of constants of derivatives of the amino-acids.

I have already stated, with numerous examples,† that the primary effect of replacing a hydrogen atom by a methyl group is in general to diminish the constant of an acid. This may be seen to be the case for the methyl derivatives of acetic acid tabulated on p. 141. Conversely, the methylation of ammonia, up to the stage of dimethylamine at least, is accompanied by increase in the value of the basic constant. One might consequently imagine the direct effect of the introduction of a methyl group into the basic radical of an amino-acid would be to increase the value of the basic constant and perhaps slightly diminish the value of the acid constant. If, however, the introduction of the methyl group increased the extent of ring-formation or brought the acidic and basic radicals into closer approximation, then the secondary stereochemical effect would be a diminution of both acidic and basic constants.‡ Since the introduction of a methyl group into a primary amine is not associated with any great increase in the value of the basic constant, we should not expect the primary effect of a similar substitution in an amphoteric electrolyte to be any great variation either of k_a or of k_b. The secondary effect of the stereochemical approximation of the active radicals might, however, be many times greater, since we know that in the case of dibasic acids the reinforcement of each carboxyl group by the other is in general much increased by the stereochemical influence of the introduction of methyl groups.§

* R. Wegscheider, 'Sitzungsber. d. kaiserl. Akad. d. Wiss. in Wien, Math.-naturw. Kl.,' vol. 114, Abt. ii, b., 1905.

† 'Chem. Soc. Journ.,' vol. 77, p. 397, 1900.

‡ Compare Winkelblech, 'Zeit. physikal. Chem.,' vol. 36, p. 588, 1901.

§ Compare Bone Sudborough, and Sprankling, 'Chem. Soc. Journ.,' vol. 85, p. 540, 1904.

Now in the three aminobenzoic acids we should expect the influence of each active radical on the other to be greatest in the case of the ortho-acid, and least in the case of the para-acid. The following table gives the constants for these substances and their methyl derivatives.

	Ortho.		Para.	
	$k_a \times 10^5$.	$k_b \times 10^{12}$.	$k_a \times 10^5$.	$k_b \times 10^{12}$.
Aminobenzoic acid.....	1·4	1·3	1·2	2·5
Monomethyl derivative.....	0·46	0·9	0·92	1·7
Dimethyl derivative	0·00023	0·28	0·94	3·2

The derivatives of the para-acid show a slight fall of the acid constant, and, from the first to the last member, a slight increase of the basic constant. Here the stereochemical effect (including change of ring-formation) seems to be almost absent, and the primary influence of the methyl groups is apparent. In the ortho series, on the other hand, we have a very distinct falling off of the acid constant in passing from the first to the second member, and an enormous diminution in passing from the second to the third. The fall of the basic constant is less well marked and more regular.

The very small value of k_a for dimethylortho-aminobenzoic acid is probably to be attributed to ring-formation.* A similar diminution in the basic constant by ring-formation need not be looked for, since the basic radical involved in the ring-formation must already, when directly attached to the benzene nucleus, be almost wholly anhydrous (compare p. 142).

The meta derivatives resemble those of the para series more closely than those of the ortho series:—

	$k_a \times 10^5$.	$k_b \times 10^{12}$.
Meta-aminobenzoic acid	1·6	13
Monomethyl derivative	0·8	12
Dimethyl derivative	0·8	19

The peculiarity which they exhibit is the comparatively great value of all the basic constants.

In the case of glycine (amino-acetic acid) we should expect the acidic and basic radicals, owing to their proximity, greatly to affect and neutralise each other. This we find very pronouncedly in the acidic constants, which have only about 1/50000 of the value of the corresponding constants of the amino-benzoic acids.

* Compare Cumming, *loc. cit.*, p. 122.

	$k_a \times 10^5$.	$k_b \times 10^{12}$.
Amino-acetic acid	0·000034	2·9
Monomethyl derivative	0·000013	1·8
Dimethyl derivative.....	0·000014	1·1

From this table it will be seen that the values of the acid constant of the amino-acetic series are even smaller than that of ortho-dimethyl-amino-benzoic acid, pointing to even more extensive ring-formation. The primary effect of the introduction of a basic radical into acetic acid could scarcely produce this reduction of the acidic constant from $1{\cdot}8 \times 10^{-5}$ to $3{\cdot}4 \times 10^{-10}$, for the introduction of an amino group into the ortho position of benzoic acid only reduces the acidic constant to about one-fourth of its former value, namely, from $C_6H_5.COOH = 6{\cdot}0 \times 10^{-5}$ to $o-NH_2.C_6H_4.COOH = 1{\cdot}4 \times 10^{-5}$.

It need scarcely be pointed out that the comparatively slight diminution of the constant of benzoic acid by the introduction of an amino group indicates the presence of little or no ring-formation in the amino-benzoic acids.

A consideration of the esters of amino-acids is, to some extent, helpful in dealing with the effect of hydration and ring-formation on the basic constants of these acids. If the carboxyl group of an amino-acid is esterised, no ring-formation is possible, *i.e.*, $R<^{NH_2}_{COOMe}$ is not convertible by solution in water into $R<^{NH_2Me}_{COO}$. By comparison, then, of the basic constants of the amino-acid and of its ester, we may obtain some information as to the state of the acid in solution.

The probable effect of the substitution of the group COOMe for the carboxyl group COOH may be ascertained from the consideration of the same substitution in dibasic acids.

I have shown elsewhere* that the substitution of COOEt or COOMe for one COOH group in a dibasic acid reduces the acid constant of the latter to approximately half its original value, provided that there is no great stereochemical influence of the two carboxyl groups in the original acid. Wegscheider,† in a theoretical treatment of the subject, deduced the relation

$$K = 2k$$

for a symmetrical dibasic acid, K being the observed acidic constant of the acid, and k the constant for each carboxyl group singly. If, therefore, the constant of the ester-acid is half that of the dibasic acid we conclude that the

* 'Chem. Soc. Journ.,' vol. 61, p. 696, 1892.

† 'Monatshefte für Chem.,' vol. 16, p. 153, 1895 ; *ibid.*, vol. 23, p. 346, 1902.

influence of the COOMe group or the COOH group on the other carboxyl group is precisely the same.

From another point of view the matter appears as follows. If the two carboxyl groups of a dibasic acid are sufficiently far apart to exert no stereochemical influence on each other, the double value of the constant of the dibasic acid is simply due to the double number of ionisable carboxyl groups in the solution, since the concentrations (or dilutions) used in calculating the dissociation constants are *molecular* and not *equivalent* concentrations (or dilutions).* In short, if we calculate with equivalent dilutions, instead of molecular dilutions, the dissociation constant of a symmetrical dibasic acid will be the same as that of a monobasic acid of the same structure. The constant of suberic acid, $COOH.CH_2.CH_2.CH_2|CH_2.CH_2.CH_2.COOH$, is $k_a = 0{\cdot}0000296$. That of butyric acid, $CH_3.CH_2.CH_2.COOH$, is 0·0000149. Now, in the expression

$$m^2/(1-m)v = 0{\cdot}0000296$$

for suberic acid, let us substitute the equivalent dilution, $v' = 0{\cdot}5\ v$, for the molecular dilution v, and we obtain

$$m^2/(1-m)v' = 0{\cdot}0000148,$$

practically identical with the acidic constant of butyric acid. We may take it, then, that the carboxyl groups in suberic acid do not reinforce each other at all.

The dissociation constant of succinic acid, $COOH.CH_2|CH_2.COOH$, is 0·000068; that of acetic acid, $CH_3.COOH$, is 0·000018, when molecular dilutions are reckoned. The constant of succinic acid, when reduced to equivalent dilution, is 0·000034. It is thus greater than that of the monobasic acetic acid, and we may legitimately infer, therefore, that the carboxyl groups in succinic acid reinforce each other considerably.

Coming now to the ester-acids, we have for hydrogen ethyl suberate, $COOEt.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.COOH$, $k = 0{\cdot}0000146$. This is almost equal to the value for an equivalent solution of suberic acid, as we might expect, since we have seen that the carboxyl groups of suberic acid do not reinforce each other, except in as far as each neutralises the slight positive effect of the extended hydrocarbon radical. This latter neutralising effect is equally well produced by the COOEt group.

* For purposes of comparison it would be better to refer throughout to *equivalent* instead of molecular concentrations, at least when the polybasic acids are symmetrical, or nearly so. Thus the Ostwald affinity constants of dibasic acids should be divided by 2 those of tribasic acids by 3, etc., for effective comparison with monobasic acids.

In succinic acid we have just seen that the carboxyl groups reinforce each other. It is therefore to be expected that in the ester acid,

$$COOEt.CH_2.CH_2.COOH,$$

the group COOEt should exert an influence on the remaining COOH group. Comparing equivalent concentrations, we have the constants:

Acid.	$k \times 10^5$.
$H.CH_2.COOH$	1·8
$COOEt.CH_2.CH_2.COOH$	3·0
$\frac{1}{2}(.CH_2.COOH)_2$	3·4

The influence of the group COOEt is here less than that of the COOH group, but only slightly less.

In general, we may say that when the carboxyl groups do not very strongly reinforce each other, the COOEt, COOMe, or COOH groups have practically the same effect on a carboxyl group. When there is very strong reinforcement, as in the case of malonic or maleïc acids, the effect of the ester group is much less than that of the carboxyl group.*

Applying these results now to the consideration of amphoteric electrolytes, we should expect that when there is no great stereochemical influence of the acidic and basic radicals on each other, the esterisation of the acid should produce little or no change in the value of the basic constant, provided, of course, that there is no change in the extent of hydration. We have already deduced that the reciprocal influence of the acidic and basic radicals in the para-aminobenzoic series is slight. There should be little difference, therefore, in the basic constants of these acids and their methyl esters.

Para Series.

	Acid. $k_b \times 10^{12}$.	Ester. $k_b \times 10^{12}$.
Aminobenzoic acid	2·5	2·4
Monomethyl derivative	1·7	2·1
Dimethyl derivative	3·2	3·3

It is evident from these figures that the theoretical requirements are closely fulfilled, and that the extinction of the acidic radical has little effect on the basic portion of the molecule.

Take, now, the ortho series, in which the stereochemical influence is greater.

* Compare Wegscheider, 'Monatshefte,' *loc. cit.*

[illegible]

	[illegible]	[illegible]
	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

Meta series.

	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]

[illegible]

	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

	$k_2 \times 10^{12}$.	$k_1 \times 10^{12}$.
Betaine	*ca.* 0·01	0·87
Ortho-benzbetaine	*ca.* 0·01	0·28
Meta-benzbetaine	*ca.* 0·01	33·9
Para-benzbetaine	*ca.* 0·01	32·3

Here, again, the stereochemical influence is evident in betaine and ortho-benzbetaine, which are much more weakly basic than meta-benzbetaine and para-benzbetaine.

The hydrated form of a betaine is $R<^{NMe_3OH}_{COOH}$, in which the basic group is quaternary and, therefore, very powerful; the acid group, on the other hand, is of the usual comparatively feeble type. Even then, though ring-formation has become so nearly complete as to bring about the practical disappearance of acid properties, the basic properties will still persist in a measurable degree, owing to the inherent strength of the free basic group. The powerfully basic character of the quaternary group is rendered evident by Dr. Cumming's observations on the autosaponification of the ester $o\text{-}C_6H_4<^{NMe_3OH}_{COOMe}$, and the action of this ester on methyl acetate,* which it saponifies at a rate comparable to that attained by an equivalent solution of caustic soda.

The chlorides and iodides of these betaine-esters were all found to possess a slightly acid reaction to azolitmin. This is at first sight surprising, since the substances themselves have no acid group, and since, with bases of such great strength, there can be no appreciable hydrolysis of their salts in aqueous solution. It must be borne in mind, however, that the substances, being esters, are liable to become hydrolysed (saponified) when dissolved in water, with production of minute quantities of the corresponding acid (betaine salt).† Now, this is the salt of such a feeble base that at small concentrations it is practically all hydrolysed into the betaine and the strong mineral acid. The traces of mineral acid thus produced would sufficiently account for the feebly acid reaction of the solutions.

Probably the methyl acetate catalysis observed with betaine ethyl ester chloride‡ is attributable to the same cause, in part at least, the observed value of k_b, viz., 10^{-11}, being probably much smaller than that of the real basic constant of betaine ethyl ester hydroxide.

* *Loc. cit.*, p. 127.
† Cumming, p. 124.
‡ Johnston, p. 100.

On the Distribution of Radium in the Earth's Crust.

By the Hon. R. J. Strutt, F.R.S., Fellow of Trinity College, Cambridge.

(Received June 20,—Read June 21, 1906.)

Part II.—Sedimentary Rocks.

In a paper read before the Society on April 5, I gave determinations of the quantity of radium in igneous rocks. Similar data for sedimentary deposits will now be given to complete my survey of the radium content of the earth's crust.

The limestones examined (oolite, chalk, marble, etc.) were simply dissolved in hydrochloric acid, and the emanation extracted from the solution. All other rocks (including sandstones, clays, slates, gravel) were first fused with sodium carbonate, in exactly the same way as the igneous rocks dealt with in the former paper. I believe that in some cases, clays for instance, this is unnecessary; for determinations made on clay simply treated with hydrochloric acid gave the full quantity of emanation.* But to avoid any doubt, fusion was always resorted to.

The results for sedimentary rocks are given in Table I.

Table I.

Rock.	Locality.	Radium per gramme, in grammes.
Oolite	Bath	$5{\cdot}84 \times 10^{-12}$
Oolite	St. Alban's Head	$4{\cdot}05 \times 10^{-12}$
Marble	East Lothian	$3{\cdot}87 \times 10^{-12}$
Kimmeridge clay	Ely	$3{\cdot}77 \times 10^{-12}$
Oil-bearing sandstone	Gallicia	$3{\cdot}04 \times 10^{-12}$
Roofing slate	Wales (?)	$2{\cdot}57 \times 10^{-12}$
Silicified gritty slate	St. Ives, Cornwall	$2{\cdot}50 \times 10^{-12}$
Gault clay	Cambridge	$2{\cdot}13 \times 10^{-12}$
Clay	Terling, Essex	$1{\cdot}73 \times 10^{-12}$
Red sandstone	East Lothian	$1{\cdot}68 \times 10^{-12}$
Gravel (fine siftings)	Terling, Essex	$1{\cdot}42 \times 10^{-12}$
Red chalk	Hunstanton	$1{\cdot}07 \times 10^{-12}$
Flint (large nodules)	Terling, Essex	$1{\cdot}06 \times 10^{-12}$
White marble	Deccan, India	$0{\cdot}54 \times 10^{-12}$
Marble	East Lothian	$0{\cdot}52 \times 10^{-12}$
Chalk	Bottom of pit, Cherry Hinton, Cambridgeshire	$0{\cdot}78 \times 10^{-12}$
Chalk†	Top of same pit	$0{\cdot}25 \times 10^{-12}$

* The emanation cannot be quantitatively extracted from clay by merely boiling it with water.

† This determination was made on 500 grammes of material, in order to get a sufficient leak for measurement.

On comparing these figures with those given in my former paper for igneous rocks,* it will be observed that the average radium content of sedimentary deposits does not differ appreciably from that of igneous rocks. This is what might be expected on the received view that sedimentary rocks derive their material from the disintegration of igneous ones.

It appears then that the examination of sedimentary rocks for radium gives no reason for altering the estimate of the radium content of the earth's crust formerly arrived at.

I have examined a few other materials which cannot be properly described as rocks, but which are of interest in the present connection.

The results are given below:—

Table II.

Material.	Radium per gramme in grammes.
Deposit from hot springs, Bath	828×10^{-12}
Cambridge tap-water†	$0{\cdot}78 \times 10^{-12}$
Sea-salt (approximate determination only)...	$0{\cdot}15 \times 10^{-12}$
Boiler crust, Cambridge.....	$0{\cdot}078 \times 10^{-12}$

It will be noticed that the deposit from the Bath spring is 100 times as rich as any rock. The materials transported by cold water, sea salt, and boiler crust are, on the other hand, much poorer in radium than any of the rocks.

Part III.—Rock-forming Minerals.

Igneous rocks are aggregates of many distinct minerals. It was felt that the enquiry as to the distribution of radium in such rocks would be incomplete without some attempt to determine in which of these minerals that element chiefly resides.

Most of the rock-forming minerals can be obtained in large well developed crystals. Such crystals occur for the most part in exceptional localities where crystallisation has been extremely slow, and where the structure of the rocks is on a large scale throughout. In these cases it is easy to obtain any desired quantity of the pure mineral for investigation.

I have examined a number of such specimens of rock-forming minerals for radium. The results are given in Table III. In some cases the quantity of material taken for the experiment proved insufficient to give a satisfactory quantitative measure of the amount of radium in the mineral. This is

* 'Roy. Soc. Proc.,' vol. 77, A, p. 479, last column but one of the table.

† This is the quantity of radium which corresponds to the emanation dissolved in 1 c.c. of the water. The radium is not itself present in the water.

indicated by a note of interrogation. In other cases no radium at all was detected. In all probability some traces would have been found if more of the mineral had been taken, but the object was to determine whether the mineral made any important contribution to the total radium in the rock. Thus it was not thought worth while to push the examination of accessory minerals, such as ilmenite or rutile, which only occur in small proportions, very far. The quantities of material taken for these experiments are given, so that the quantitative significance of a negative result may be judged.

Table III.

Mineral.	Locality where found.	Quantity taken, grammes.	Radium per gramme, in grammes.
Zircon	Ural Mountains	1	865×10^{-12}
Zircon	North Carolina	1	658×10^{-12}
Zircon	Brevig	0·690	139×10^{-12}
Zircon	Kimberley	1·17	$74·8 \times 10^{-12}$
Perofskite	Magnet Cove, Arkansas	1	197×10^{-12}
Sphene	?	1	102×10^{-12}
Apatite	Sweden	8	$29·7 \times 10^{-12}$
Apatite	California	4·7	$11·0 \times 10^{-12}$
Hornblende	?	7·5	$4·27 \times 10^{-12}$
Tourmaline	Devonshire	11·3	$3·32 \times 10^{-12}$
Labradorite	Labrador	17	$1·1 \times 10^{-12}$?
White felspar	Nellore, India	20	$0·6 \times 10^{-12}$?
White mica	Nellore, India	10	$1·0 \times 10^{-12}$?
Brown mica	Deccan	10	$1·0 \times 10^{-12}$?
Brown mica	?	10	Nil.
White quartz	Nellore, India	30	Nil.
Rutile	?	1	Nil.
Ilmenite	?	1	Nil.

It will be observed that certain of the accessory minerals, *i.e.*, zircon, sphene, perofskite and apatite, which occur in granite, are rich in radium. The hornblende, micas, tourmaline and felspars examined contain much less, while in quartz none could be detected.

Although these experiments throw a certain amount of light on the subject, they are in some respects inconclusive. It is not safe to take these exceptional cases where large crystals occur, as typical; for slow crystallisation is likely to result in more perfect separation of the constituent elements. Moreover, it is difficult to form any idea of the proportion in which the various minerals occur, especially when there has been no opportunity of examining them *in situ*. One cannot tell, for instance, whether enough zircon occurs to account for any large fraction of the radium contained in the whole rock. I have accordingly made some experiments by separating the constituents of an ordinary rock. For this purpose Cornish granite was

selected, as being comparatively rich in radium, and coarse enough to allow of easy separation of the constituent minerals. Sixty-five grammes of Cornish granite was powdered just so far that each particle was seen to be composed of one mineral only, when examined with a magnifier. Bromoform was used to separate the dense minerals from the light ones. The dense minerals, which sank, weighed only 7·5 grammes. The rest of the powder, consisting of quartz and felspar, floated on the liquid.

The dense portion consisted mainly of brown mica, but may have contained some zircon enclosed between the flakes, the separation of which by mechanical methods would be impracticable. The dense portion was accordingly digested with hydrochloric acid until the flakes had lost all their colour, nothing but silica remaining. This treatment would leave the zircon behind, as it is not appreciably acted on by hydrochloric acid.

The rock was thus divided into three portions. The quantity of radium in each of these portions was determined by the usual method.

The result was that 1 gramme of Cornish granite contains :—

	Radium.	
In the light portion (quartz and felspar).....	$3{\cdot}85 \times 10^{-12}$	gramme.
In the heavy portion, soluble in HCl (brown mica) ...	$4{\cdot}27 \times 10^{-12}$	„
In the heavy portion, insoluble in HCl (zircon ?)	$1{\cdot}02 \times 10^{-12}$	„
Total	$9{\cdot}14 \times 10^{-12}$	„

It appears therefore that more than half of the radium is contained in the heavy minerals, though these are only 1/8 of the whole mass of the rock. Although the separation by means of bromoform was not perfect, it was, I think, good enough to make it certain that a considerable portion of radium is really contained in the light constituents. As to the heavy minerals, it would not seem that there is enough zircon to account for much of the radium, which chiefly resides in the brown mica.

It appears that radium, or rather its parent, uranium, is not perfectly separated from a rock magma by the crystallisation of the heavy constituents, though considerable concentration in these constituents occurs.

On the Ultra-Violet Spectrum of Ytterbium.

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Received June 21,—Read June 28, 1906.)

The rare earth, ytterbia, was discovered in 1878 by Marignac.* In 1880 Nilson,† in purifying Marignac's ytterbia, found that it contained another earth which he named scandia. Cleve, and more recently his daughter Astrid Cleve, have worked much on ytterbia, and within the last few years M. Urbain has taken up the subject, and has succeeded in purifying ytterbia in larger quantities. During my own work on the fractionation of the rare earths I also have prepared and worked with ytterbia.

Marignac, Nilson, Cleve, and Urbain have each presented me with some of their ytterbia. Nilson's earth, sent in 1886, appears very pure. Unfortunately, there was only sufficient to enable me to photograph the part of its spectrum between wave-lengths 2400 and 2580.

Ytterbia is one of the least basic oxides of the yttria group; the order being yttria, erbia, thulia, ytterbia, and scandia; yttria being the most basic and scandia the least. The atomic weight of ytterbium, taking the formula of the oxide, the only one known, as Yb_2O_3, is, according to Nilson, 173·01. Miss Astrid Cleve obtained the number 173·11. The salts of ytterbium are colourless and show no spectrum bands by transmitted light.

My ytterbia was prepared from the mixed yttria earths by the old method of partial decomposition of the nitrates by heat. The chief difficulty is to free the ytterbia from the last traces of thulia. The fractionation of the nitrates must go on until a considerable thickness of the fused nitrate shows no trace of the thulium absorption bands at wave-lengths 4700 and 7000. A trace of scandia may still be present, but this earth is very seldom met with. All my tests have failed to show its presence, and Miss Cleve, working with several kilogrammes of ytterbium earths derived from different minerals, also was unable to find scandium in them.

In April, 1904, M. Urbain gave me sufficient of his purest ytterbia to enable me to photograph its complete ultra-violet spectrum. His earth was prepared by the fractional crystallisation of the ethyl-sulphates of crude gadolinite earths.‡ The subsequent separation is by the fusing nitrate method. This after 20 series of fusions gave in the least basic portions a mixture of

* 'Comptes Rendus,' vol. 87, p. 578.

† 'Ber.,' vol. 12, p. 554.

‡ 'Comptes Rendus,' vol. 132, p. 136.

ytterbia and thoria, which are easily separated by Wyrouboff and Verneuil's method. This is the ytterbia of which I have photographed the spectrum. It still contains traces of thulia. M. Urbain's more recent method of preparing ytterbia is by fractionally crystallising the nitrates from a slightly diluted nitric acid. In this way he tells me he has succeeded in getting ytterbia free from thulia.

The examination for absorption bands in a strong solution is a fairly good test for an earth, such as erbia and thulia, giving absorption spectra, but it is not so delicate as an examination of the spark spectrum photographed through a quartz train, for dominant lines, which most elements show in some part of their spectrum. For instance, the dominant lines of yttrium are at wave-lengths 3600·9, 3710·4, 3774·5, 4177·7, and 4375·1. The dominant lines of erbium are at 3499·3, 3692·8, and 3906·5. They are, however, not strong, and fortunately the absorption bands of this element are striking and characteristic. The spark spectrum of thulium has only been slightly examined by me, and I do not think it has any strong lines. Its absorption spectrum, as with erbium, is a very characteristic one. The spark spectrum of ytterbium has strong dominant lines at 3289·5 and 3694·4. Scandium has dominant lines at 3572·7, 3614·0, 3630·9, 3642·9, and 4247·0.

The spark spectrum of ytterbium was first examined by Thalen, but only in the visible portion. Exner and Haschek have published a set of measurements of the spark spectrum of ytterbium from wave-lengths 2116—4726.* I have found them to be very accurate, and in my photographs I have generally adopted their figures. Occasionally lines are in their list which appear to belong to other elements, and in some cases lines given by them cannot be distinguished in my spectrum.

My photographs were taken with the quartz apparatus already described, the spectrum of pure iron being used as a standard. The ytterbium spark was taken from a strong solution of the nitrate between platinum poles, sufficient self-induction being introduced to eliminate nearly all the air lines. The ytterbium, by this very severe spectrum test, is seen to be not absolutely free from impurities—thulium,† copper and calcium, being present. Thulium

* 'Wellenlängen-Tabellen für Spektralanalytische Untersuchungen,' F. Deuticke, Leipzig und Wien, 1902.

† M. Urbain writes, under date May 5, 1906 :—"The ytterbium, of which you have taken the spectrum, was prepared some years ago. It is impossible to affirm that it does not contain thulium, and the experience I have acquired since these already ancient researches leads me to think it does contain traces. Thulium is very difficult to separate completely from ytterbium, and I have only recently succeeded in doing so. Do not fail to mention that this preparation was obtained by fusion of the nitrates of the rose-coloured yttric earths obtained in the tails of the crystallisation of the ethyl-sulphates."

is seen by its lines at 3020·7, 3131·4, 3425·2, 3441·6, 3462·4, and 3848·2. Copper is seen by its dominant lines at 3247·7 and 3274·1, and calcium by its dominant lines at 3933·8 and 3968·6.

The platinum lines which are present are easily recognised, and are useful as an additional measure of identification. Besides these, a number of fainter and indistinct lines are seen. These may be due to ytterbium or to traces of hitherto unrecognised impurities.

The wave-lengths of all the recognisable lines of ytterbium are given on the photograph, and also those of thulium, calcium, and copper, but the platinum lines are not marked.

A Method for Determining Velocities of Saponification.

By Professor JAMES WALKER, F.R.S.

(Received July 10, 1906.)

(From the Chemical Laboratory, University College, Dundee.)

A possible method of following the progress of a reaction in which electrolytes are involved is to measure the electrical conductivity of the solution at stated intervals. This method was employed by Walker and Kay* in their investigation of the conversion of ammonium cyanate into urea, and is capable of a more extended application.

The chief conditions for the convenient application of the method are: first, that there should be a considerable difference in conductivity between the initial and final systems, and second, that the change in conductivity should be proportional to the progress of the reaction. It occurred to me that these conditions would be well fulfilled in the saponification of an ester by a caustic alkali. The conductivity of the alkali, say sodium hydroxide, is much greater than that of the sodium salt produced by the saponification, owing to the high velocity of hydroxidion as compared with the salt anion. Since, too, sodium hydroxide and sodium salts of monobasic acids are approximately equally ionised under the same conditions, the ionisation in dilute solution remains practically the same throughout the saponification, and thus the alteration in the conductivity is almost exactly proportional to the progress of the reaction.

The following experiment on the rate of saponification of methyl acetate by caustic soda may be quoted as an example of the method carried out under ordinary laboratory conditions with the apparatus generally used for conductivity measurements in solution.

The conductivity cell used was of the narrow Arrhenius type, and was immersed in a thermostat at 25°. In this cell were placed 4 c.c. of N/20 caustic soda, and 15 c.c. of water. To prevent access of carbon dioxide, the hole in the ebonite cover was plugged with a small rubber stopper. When the temperature of the thermostat had been reached, the solution was stirred by raising and lowering the electrodes, and the conductivity was read off. To the solution was then added 1 c.c. of N/5 solution of methyl acetate, the time being simultaneously noted, and the contents of the cell were well stirred by up-and-down motion of the electrodes. A reading of the conductivity was

* 'Journ. Chem. Soc.,' vol. 71, p. 489, 1897.

at once taken after mixing, but this acted merely as a check, and was not used in the calculation. After a short interval readings were made of the conductivity of the solution (which was now N/100, both with regard to sodium hydroxide and to methyl acetate), at first every minute, and then every few minutes, when the reaction had become slower.

The following table contains the results of the observations. In it a represents the bridge reading, and x the difference between the initial value of $a/(1-a)$, which is proportional to the conductivity, and the value after t minutes.

t.	$a/(1-a)$.	x.	$\frac{1}{t} \cdot \frac{x}{1-x}$.
0	(1·564)	0	—
3	1·304	0·260	0·117
4	1·247	0·317	0·116
5	1·198	0·366	0·115
6	1·153	0·411	0·116
7	1·114	0·450	0·117
8	1·083	0·481	0·116
10	1·026	0·536	0·115
12	0·980	0·584	0·117
15	0·927	0·637	0·117
18	0·883	0·681	0·118
21	0·852	0·712	0·118
25	0·818	0·746	0·118
∞	(0·564)	(1·000)	Mean 0·118

It will be noticed that the constant for the bimolecular reaction is here very satisfactory and in general it may be said that the maximum divergence from the mean value does not exceed 1 to 2 per cent. It is, however, advisable to neglect the first and last fourths of the reaction, since in them initial disturbances and the effect of a slight departure from exact equivalence of the reacting substances have a relatively large effect on the value of the constant.

The initial reading of the conductivity cannot be taken directly, owing to the great speed of the reaction. In order to obtain it, the conductivity of the alkaline solution is read before the methyl acetate is added. In the above instance the conductivity read in this way is that of a solution N/95 with regard to sodium hydroxide, 4 c.c. of N/20 solution being contained in 19 c.c. When this is diluted to N/100 by the addition of 1 c.c. of the methyl acetate solution, the conductivity will fall off in the ratio of 100 to 95, since the quantity of methyl acetate in the solution after mixing is less than 0·1 per cent., and can have no appreciable effect either on the speed or the number of the ions. From the conductivity of the solution before addition of the

methyl acetate we therefore deduct one-twentieth of its value in order to obtain the initial conductivity after mixing.

The final reading may of course be ascertained by waiting till the action has ceased, but it is both more expeditious and more accurate to measure the conductivity of a N/100 solution of sodium acetate prepared by neutralising the N/20 solution of caustic soda by means of acetic acid and diluting to the requisite extent. It is well to make this measurement of the end-point before beginning the actual saponification. Theoretically the end-point can be calculated from the initial reading and the known ratio of the conductivities of N/100 solutions of sodium hydroxide and sodium acetate, but it is advisable to perform the experiment as a check.

The calculation of the constant $\frac{1}{t} \cdot \frac{x}{1-x}$ may be much simplified by the following device. For conductivity work a table is used which gives the ratio $a/(1-a)$ for different values of the bridge-reading a. If therefore, we make the total range of the reaction equal to unity, we can use the same table to obtain the ratio $x/(1-x)$ and have then merely to divide by the time t, a calculation which can be performed mentally if the intervals are suitably chosen. Now it is always possible to make the range between the initial and final values of $a/(1-a)$ equal to unity by introducing the appropriate resistance in the resistance box. Thus in the above example it was found that the ratio between the initial and final conductivities was 2·773 : 1. We have then $i/f = 2{\cdot}773$, and we wish to make $i-f = 1$. From these two equations we obtain $i = 1{\cdot}564$ and $f = 0{\cdot}564$. We have therefore so to adjust the resistance that the initial value of $a/(1-a)$ shall be 1·564. This refers to the N/100 solution after mixing, whilst the conductivity actually measured is that of a N/95 solution. We must therefore increase the value 1·564 in the ratio of 100 to 95, and thus obtain 1·646 as the value of $a/(1-a)$ which the N/95 solution of caustic soda must exhibit if the difference between the initial and final values of $a/(1-a)$ is to be unity. In the table this value of $a/(1-a)$ corresponds to $a=0{\cdot}622$. We therefore adjust the resistance in the box, either by trial or by calculation, until the minimum for the N/95 solution of caustic soda is exactly at this part of the bridge, and then proceed with the experiment. This adjustment, though tedious in description, only occupies a few minutes in practice, and saves much time in the subsequent calculations. Even if readings are taken every minute, the calculation of the constant $\frac{1}{t} \cdot \frac{x}{1-x}$ from each observation can be performed in the interval between two readings, generally without the necessity of putting pen to paper.

To obtain the velocity constant from the mean value of $\frac{1}{t} \cdot \frac{x}{1-x}$ it is only necessary to divide by the normality of the solution. In the above instance the velocity constant is thus 0·117 ÷ 0·01 = 11·7.

As a further example of the method, I append a series of observations made by Mr. D. C. Crichton, B.Sc., on the velocity of saponification of ethyl acetate by caustic soda at 24°·85, the concentration of both substances being N/100.

t.	$a/(1-a)$.	x.	$\frac{1}{t} \cdot \frac{x}{1-x}$.
0	(1·560)	0	—
5	1·315	0·245	0·0649
7	1·247	0·313	0·0651
9	1·193	0·367	0·0645
11	1·146	0·414	0·0642
13	1·101	0·459	0·0652
15	1·064	0·496	0·0650
18	1·020	0·540	0·0652
20	0·994	0·566	0·0652
25	0·945	0·615	0·0642
27	0·923	0·637	0·0650
33	0·880	0·680	0·0644
37	0·756	0·704	0·0644
∞	(0·560)	(1·000)	Mean 0·0647

The velocity constant of the saponification of ethyl acetate by caustic soda at this temperature is therefore 6·47, a value in exact accordance with the curve which expresses the results of Warder* and of Reicher† obtained by the titration method.

The conductivity method, even without special apparatus, is at least as accurate as the titration method carried out under specially favourable circumstances, and for rapid reactions is incomparably less trying in execution.

* 'Amer. Chem. Journ.,' vol. 3, p. 203, 1881.

† 'Liebig's Annalen,' vol. 232, p. 103, 1886.

The Tidal Régime of the River Mersey, as Affected by the Recent Dredgings at the Bar in Liverpool Bay.

By JAMES N. SHOOLBRED, B.A. (Lond.), M.Inst.C.E.

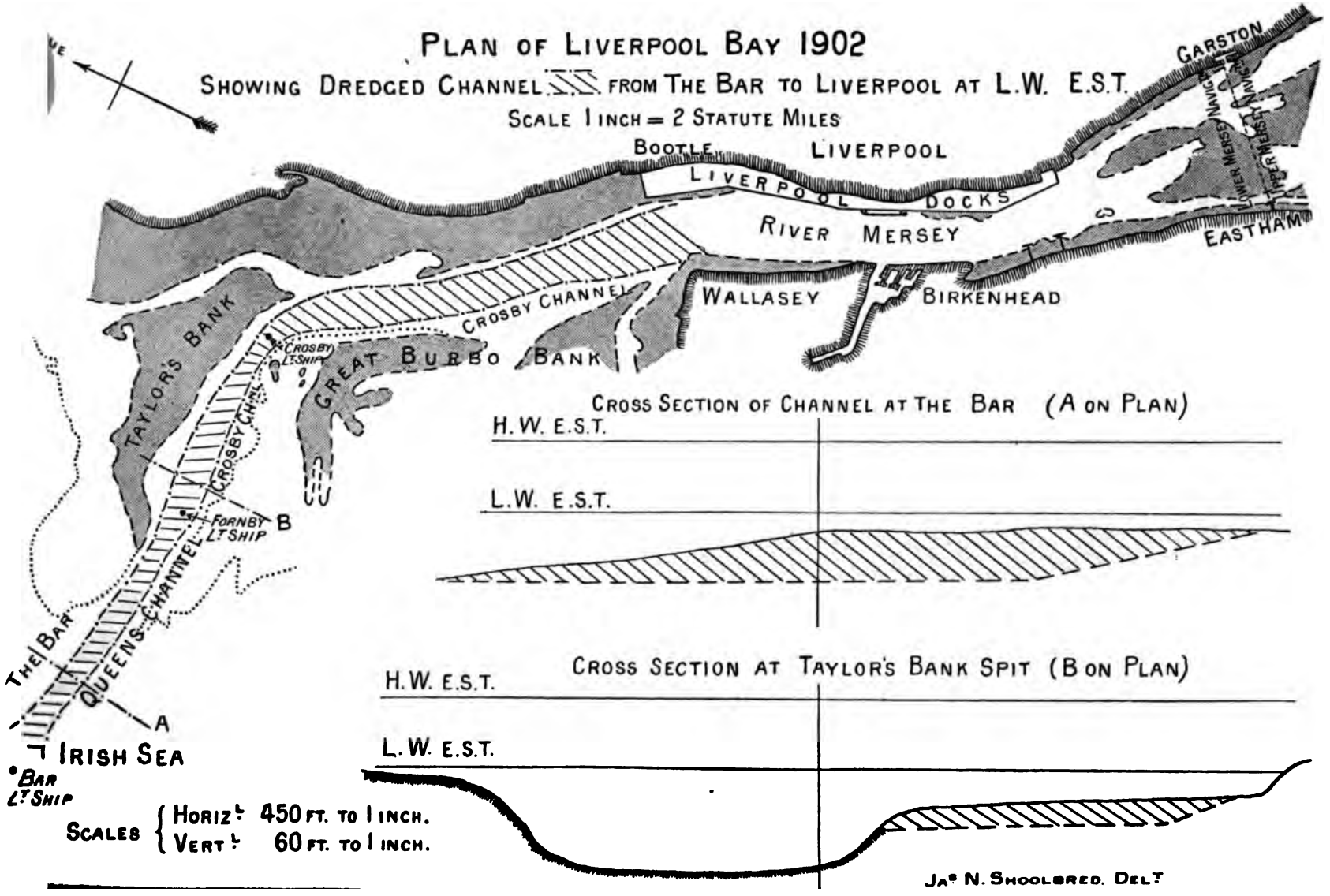
(Communicated by Lord Kelvin, F.R.S. Received May 30,—Read June 28, 1906.)

Liverpool, the premier port of the world after our metropolis, with the annual total of in-and-out tonnage, in 1904, of 32 millions of tons, had suffered, in the approach thereto, up to about 15 years ago, from a sand-bar, situate at the outer or seaward entrance into Liverpool Bay, which afforded a depth of water over it, at low water of equinoctial springs, of only ten feet. When it is borne in mind that some of the large Atlantic liners have a draft of close upon 30 feet, it is easy to conceive the amount of inconvenience, chiefly by loss of time in enforced waiting outside the Bar, which this caused—a period of waiting, which affected more or less, according to their individual tonnage, all vessels visiting the port.

Attempts were made as far back as 1838 by the then Marine Surveyor of the Port of Liverpool, Lieutenant (afterwards Admiral Sir) H. T. M. Denham, to diminish the height of the Bar, by first harrowing the sand and then removing the loosened material by means of bucket-dredgers. After some years, however, it was found advisable to abandon these operations, since the effect thereof upon the Bar was so slight that a single storm from the Irish Channel often more than counteracted any deepening at the Bar, which had been effected by months of dredging. It was not, however, till shortly before 1890, that the late Mr. G. F. Lyster, then Engineer to the Mersey Docks and Harbour Board, was able to resume the attempt to remove any material at the Bar, by calling to his aid the newly invented form of sand-pump dredger, which by means of exhaust suction displaced the material in a semi-liquid state with such rapidity as to cause very sensible progress to be made in the removal of the material.

These preliminary experiments having proved sufficiently successful, in 1890 the problem of the removal of the Bar was vigorously attacked. At the end of ten years the problem was practically solved, so far as the cause of delay to incoming vessels entering the Port of Liverpool was concerned, since a minimum depth at the Bar of 26 feet of water at low water of equinoctial spring tides had been secured, or a gain of 16 feet of water over the conditions which prevailed in 1890.

Dredgings, however, are still continued; not merely at the Bar itself, but


PLAN OF LIVERPOOL BAY 1902
SHOWING DREDGED CHANNEL FROM THE BAR TO LIVERPOOL AT L.W. E.S.T.
SCALE 1 INCH = 2 STATUTE MILES
BOOTLE
LIVERPOOL
LIVERPOOL DOCKS
RIVER MERSEY
GARSTON
LOWER MERSEY NAVIGATION
UPPER MERSEY NAVIGATION
EASTHAM
WALLASEY
BIRKENHEAD
CROSBY CHANNEL
CROSBY L.T.SHIP
GREAT BURBO BANK
TAYLOR'S BANK
CROSBY CHANNEL
FORNBY L.T.SHIP
B
THE BAR
QUEENS CHANNEL
A
IRISH SEA
BAR L.T.SHIP
SCALES { HORIZ.L 450 FT. TO 1 INCH. VERT.L 60 FT. TO 1 INCH.
CROSS SECTION OF CHANNEL AT THE BAR (A ON PLAN)
H.W. E.S.T.
L.W. E.S.T.
CROSS SECTION AT TAYLOR'S BANK SPIT (B ON PLAN)
H.W. E.S.T.
L.W. E.S.T.
JAS N. SHOOLBRED. DELT

throughout the entrance channels right up to Liverpool, in the vicinity of the landing stage, so as to enable the largest Atlantic liners to make use, at any state of any tide throughout the year, of the entire length of this waterway, 16 miles, which at night is illuminated by gas-lit buoys.

The total of the dredging operations by which the above results have been arrived at between 1890 and the present time may be thus summarised :—

Dredgings, at the Bar, 35 million tons of sand; in the estuary channels 50 million tons; in the river itself 15 millions; making a total of 100 million tons. This has provided a channel at the Bar with a minimum width of 1500 feet and a depth throughout, at low water equinoctial spring tides, of 28 feet, from the Irish Sea right up to the Liverpool Landing Stage, thus forming a worthy approach to this most important port. (See the accompanying plan and cross sections of dredged channel in Liverpool Bay.)

The British Association for the Advancement of Science, which has for the last thirty years, or more, paid considerable attention, by means of committees and in other ways, to the tides in the Mersey and in the Irish Sea, and inclusive of the Harmonic Analysis of the resulting records, naturally desired to ascertain whether, and to what extent, the extra facilities afforded at the deepened Bar to the ingress and egress of the tidal current had in any way caused any alteration in the tidal curves—primarily at Liverpool, and also at other points throughout the tidal establishment of the river, that is, between the Bar and Warrington.

With this object, a Committee of the Engineering Section of the British Association was appointed at the recent Southport meeting, consisting of Lord Kelvin, F.R.S. (Chairman), and Professors Sir George Darwin, F.R.S., Osborne Reynolds, F.R.S., Hele-Shaw, F.R.S., and W. Cawthorne Unwin, F.R.S., together with the writer, as Secretary. That Committee presented their report at the succeeding meeting at Cambridge, in 1904. They reported that by means of a large number of documents, tidal-curve records, etc., which the Mersey Docks and Harbour Board had placed at their disposal, they had found, with the co-operation of Mr. Edward Roberts, of the Nautical Almanac Office, as to the Harmonic Analysis :—

(*a*) That in the principal factors in the Harmonic Analysis of the tidal-curves of 1902 at Liverpool itself there appeared to be no appreciable difference from the similar data which had been presented by Sir George Darwin, F.R.S., to the Royal Society in 1885, and in 1889.

(*b*) That a comparison of the tidal curves of the equinoctial springs and neaps of the vernal equinox, in 1893 and in 1903, at Liverpool and at six other points on the river showed that no material change had occurred during that interval, either in the range of the tide or in the form of the

curve; but that in the extreme upper reaches of the narrow fluvial portion near to Warrington the tidal stream set in earlier, and remained somewhat later during the ebb, in 1903 than in 1893.

The object of the present communication is to submit the comparative diagrams of the tidal curves, in 1893 and in 1903, at the seven localities above referred to, which cover the entire tidal establishment of the Mersey, and to do this, not merely at the vernal equinoctial spring tide, and at its corresponding equinoctial neap, as was done in the British Association Committee's Report, but to extend the comparison so as to show by means of the continuous tidal curve, which occurred in 1893, and also in that of 1903, during the whole fortnight of the vernal equinox, there have been prepared likewise similar continuous tidal curves for the fortnight of the autumnal equinox in both of the above years.

The result of this lengthened comparison of the tidal curves is that thereby may be seen the gradual progress, at each corresponding period, in the alteration in the times of high water and of low water, and also in the additional tidal water now introduced at certain periods into the upper reaches of the river. There is also brought out the relative value of the varying and progressive effects at the different points of the river. Diagrams (not here reproduced) indicate that, at the four points lowest down the river (see accompanying plan), viz., the Bar (Helbre Island), Liverpool (George's Pier), Eastham (entrance to the Manchester Ship Canal), and Garston Docks, on the opposite Lancashire shore (at all of which places the full range of all tides is felt), there is but little, if any, difference between the tidal curves of 1893 and of 1903, that is, before the dredging operations were actively commenced, and the date when the present increased depth of channel was attained.

A line drawn across the river from Garston to Eastham forms the imaginary division between the Lower and the Upper Mersey navigations. The former, with its total navigable length from the Bar of 20 miles, obtains therefore the full advantage for the Port of Liverpool of the complete range of all tides. This is a matter of the utmost importance, since of the 32 millions of the tonnage of the shipping in and out of the Mersey, in 1904, no less than 28 millions were confined to the Lower Mersey, while of the balance of 4 millions in the Upper Mersey, 3¼ millions went up the Ship Canal to Manchester, and the remainder to Widnes and to Ellesmere Port. All the larger steam and sailing vessels entering the Mersey, with but a few exceptions which go to Manchester by the Ship Canal, make the Port of Liverpool their destination.

From the connecting line between Eastham and Garston above referred to,

as dividing the Lower and the Upper Mersey Navigations, the bed of the River Mersey rises rapidly, through what is known as the Upper Estuary, to Runcorn Bridge, joining the towns of Widnes and Runcorn; throughout a distance of nearly 11 miles of the wide, sandy Upper Estuary there is an average rise of 18 inches per mile in the river bed. From Runcorn Bridge to Warrington, somewhat over nine miles, where the river partakes more of the character of an inland stream, the rise in the bed is not so steep, having an average gradient of but 12 inches per mile.

The effect of this steep rise in the river bed upon the tides, and particularly upon the range thereof, is very marked. Throughout the entire length of the Lower Mersey Navigation of 20 miles, the full range of each tide is available. This may be taken as 31 feet on equinoctial springs, and as 10 feet on equinoctial neaps; the high water of the former tide rises to 21 feet above the "Old Dock Sill" at Liverpool, and the latter reaches there to 10 feet above the same level. This "Old Dock Sill" datum-level has been in use, in this part of the Irish Sea, for the last 150 years at least, and the more recent, but more generally known, "Ordnance Datum" or "Mean Tide Level at Liverpool" is usually taken at 4·7 feet (4′ 8″) above the "Old Dock Sill."

At Widnes, however, the range on the same springs is reduced to 14′ 6″, and for the neaps to 9 feet; while at Warrington, those springs have barely 9 feet of range and at the neaps in 1893 it was practically nil. But in 1903 these weak tides are much more visible at Warrington, though their influence is distinctly felt at Fiddler's Ferry, five miles lower down the river.

The effect of the up-hill gradient upon the rising tide is further shown in the additional height to which the high waters reach in the upper portions of the river. Thus at Widnes the equinoctial springs and neaps respectively reach a level of 1 foot at springs, and of 3 feet at neaps, higher than at Liverpool; while at Warrington the corresponding levels are, on an average, higher by 3 feet at springs, and by 7 feet at neaps than at Liverpool.

The result, therefore, of the examination of the continuous curves, each extending over a fortnight, does but confirm the conclusions of the Committee of the British Association, based upon the curves of the equinoctial springs and neaps only, that but little, if any, changes occur in the tidal conditions which prevail in the "Lower Mersey," and which affect the Port of Liverpool itself, consequent upon the recent dredgings at the Bar; this lower portion of the river being by far the most important as far as the interests of navigation are concerned.

Respecting the upper reaches of the river, near to Warrington (where, however, the navigation is not of much importance), these fortnightly con-

tinuous tidal curves show that there now remains in the river, between the respective high waters, a considerable body of water, more than there used to be before the dredgings at the Bar took place—an advantage, no doubt, to the local navigation. This increase in the amount of water appears more clearly upon these fortnightly continuous curves in the interval between the equinoctial springs and neaps than at the times of maximum and minimum range respectively of the tides. It is not possible, however, to arrive at any definite statement of the correctness, generally, of this effect without a careful examination of all of these fortnightly periods, throughout the entire year, since during each of these periods the strength of the tidal force would vary from that of its immediate predecessor, or successor.

The following table may prove of interest in connection with the above remarks, and as confirming the statement as to the small amount of change which has taken place in the tides at Liverpool during the last 50 years:—

Comparison of Harmonic Analyses of Tidal Observations at Liverpool.
53° 24′ Lat. N., 3° 0′ Long. W.

	Mean of 1857—60.*	Mean of 1866—70.*	1902.†
Principal Solar Series—			
S_1 H	0·066	0·038	0·003
S_1 κ	62	83	97
S_2 H	3·240	3·101	3·188
S_2 κ	11	12	11·32
S_4 H	0·056	0·058	0·043
S_4 κ	316	313	307·4
Principal Lunar Series—			
M_1 H	0·020	0·039	0·032
M_1 κ	258	336	345·5
M_2 H	10·100	9·881	10·091
M_2 κ	326	327	326·45
M_3 H	0·124	0·097	0·111
M_3 κ	324	324	319·0
M_4 H	0·702	0·683	0·657
M_4 κ	222	223	224·2
M_6 H	0·211	0·184	0·180
M_6 κ	348	350	353·6
M_8 H	0·077	0·061	0·052
M_8 κ	271	285	248·6

* Communicated to the Royal Society, in 1885, by Sir G. H. Darwin, F.R.S. ('Roy. Soc. Proc.,' vol. 39, p. 135).

† Computed by Mr. Edward Roberts, F.R.A.S. (Nautical Almanac Office).

Of the constants κ and H, the angles "κ" are referred to the meridian of Greenwich, and denote the lag of the tide; the "H's" are in feet and decimals thereof, and indicate the semi-tidal range.

The mean tidal level for 1902 = 4·952 feet above "Old Dock Sill."

Ionic Velocities in Air at Different Temperatures.

By P. PHILLIPS, B.A., M.Sc., 1851 Exhibition Scholar of the University of Birmingham.

(Communicated by Professor J. J. Thomson, F.R.S. Received June 7,— Read June 21, 1906.)

The object of this paper is to find at different temperatures the velocity in an electric field of the ions produced by Röntgen rays in air at atmospheric pressure. The different values obtained will tell us whether the masses of the ions depend in any way upon the temperature.

Langevin,* in 1902, described a new method which he had devised to determine the velocities of ions in an electric field. The principle of the method is as follows:—

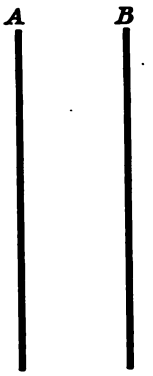


FIG. 1.

A and B are two parallel plates distant d apart. A can be earthed or connected to one pair of quadrants of an electrometer and B can be raised to a given potential, and at any instant that potential can be reversed.

With B at a given positive potential, a single discharge is sent through a Röntgen bulb which ionises the air between A and B. Let us suppose that the ionisation is uniform. At a certain time t after the discharge has passed in the bulb, the potential on B is reversed.

If we represent by a curve the quantity received by A when t is altered we shall get a curve of the form given in fig. 2. By varying the time t and measuring the quantity received by A

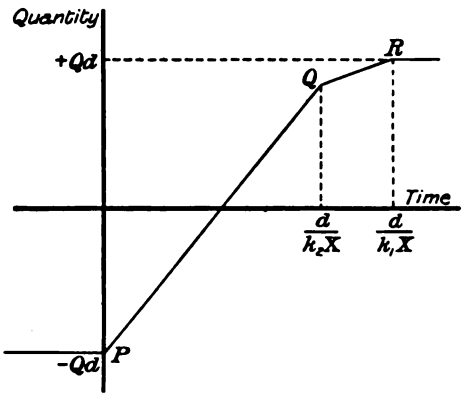


FIG. 2.

* Langevin, 'Recherches sur les gaz ionisés,' Paris, 1902.

we can experimentally realise this curve and so obtain the points of discontinuous curvature, P, Q, and R. The time between P and Q is d/k_2X and between P and R is d/k_1X, where k_1 and k_2 are the velocities under unit field of the positive and negative ions respectively, and X is the field. Knowing t, X, and d, we calculate k_1 and k_2.

If the ionisation be not uniform but be localised close to one of the plates, the form of the curve will be altered.

Suppose the ionisation is very intense close to A and that before reversal B is positive, then the form of the curve will be that given in fig. 3, while, if B is negative before the reversal, the form will be that given in fig. 4.

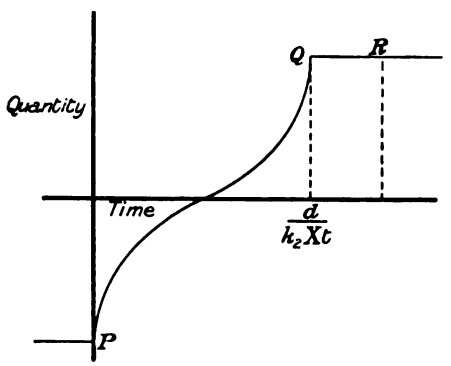


FIG. 3.

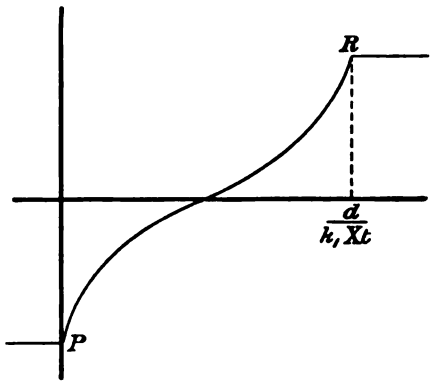


FIG. 4.

We see that in the first case the point Q of discontinuous curvature is very marked and in the second case R is very clearly marked. Using localised ionisation in this way we can find the points with greater precision.

In this investigation we have neglected the effect caused by diffusion and recombination of the ions and by the distortion of the field due to unequal distribution of the ions.

Langevin, in the thesis already referred to, has shown that diffusion and recombination only round off the corners on the curve and do not displace them; consequently the experimental curve will inform us whether these are serious. Langevin also shows that the distortion of the field is negligible if the total charge received by the plate A is less than a quarter of the charge induced on A when the potential on B is raised from zero to the potential used in the experiment. In my experiments this fraction never rose above one-twentieth.

The general arrangement of the apparatus, by means of which this method was experimentally realised, is shown in fig. 5, and is essentially the same as that described by M. Langevin.

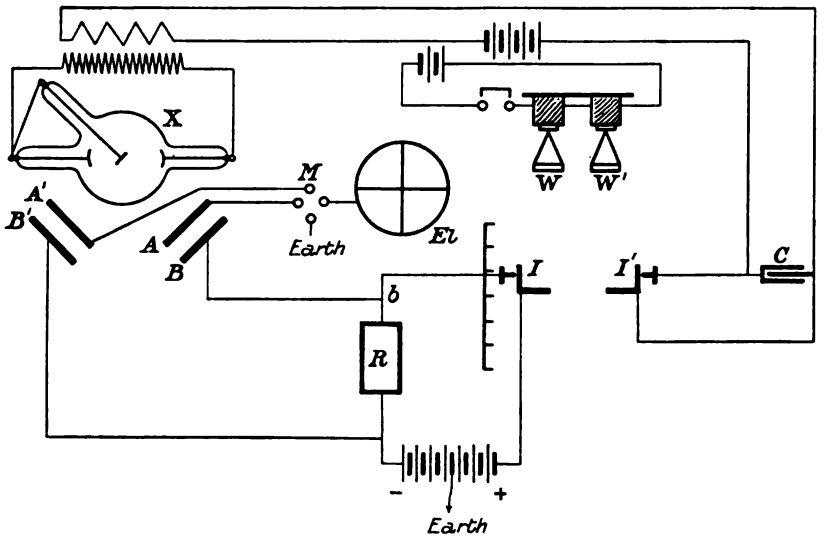


FIG. 5.

W and W′ are two weights which can be allowed to fall simultaneously and break the contacts I and I′. The breaking of the contact at I′ causes a single discharge to pass through the Röntgen bulb X, while the breaking at I reverses the potential on the electrode B.

I can be fixed at any point on a vertical scale, and thus the contact may be broken at any required time before or after it is broken in I′. As in M. Langevin's experiments, a standard pair of electrodes, A′B′, is used, and the ratio of the charge received by A to that received by A′ is the quantity which is plotted against the time in order to obtain the experimental curves.

For a fuller account of the apparatus, *vide* Langevin's thesis.

When the ionisation used is intense close to one of the plates, as in figs. 3 and 4, a null method may be used. A′B′ are so adjusted that when we travel along the horizontal parts of the curve, A′ receives an equal and opposite charge to A. A and A′ are connected together and to the electrometer, and so, while we remain on the horizontal part of the curve, we shall get no deflection, but as soon as we get beyond P, Q, or R, as the case may be, we shall get a deflection.

This is a very convenient and quick method of obtaining the position of the points, and it is used in most of the experiments described in this paper.

The electrometer has a fine phosphor-bronze suspension, gives 496 mm. deflection for 1 volt between the two pairs of quadrants, and has a capacity of about 61·5 cm.

It was found convenient to use different forms of vessel at different

temperatures, and so the description of the vessel in which A and B are enclosed will be reserved for the account of the experiments at the various temperatures.

The experiment has been carried out at the following temperatures absolute:—94°, 209°, 285°, 333°, 348°, 373°, 383°, 399°, and 411°, *i.e.*, at temperatures ranging from −179° C. to +138° C.

Between −64° C. and +138° C. the velocities of both the positive and negative ions are very nearly directly proportional to the absolute temperature, but at −179° C. the two velocities seem to be equal and much smaller than would be given by this linear law.

Determination of the Velocities at the Temperature of Boiling Liquid Air.—In order to reduce the size of the ionisation vessel as much as possible the plane parallel electrodes were replaced by concentric cylindrical ones. This slightly alters the calculation. Let the diameter of the outer cylinder be b, of the inner a.

Then at a point between a and b distant r from the centre the electric intensity is equal to $\frac{1}{r} \cdot \frac{V}{\log b/a}$, where V is the difference of potential between a and b. The velocity of the positive ions at this point will be

$$\frac{dr}{dt} = k_1 \frac{1}{r} \cdot \frac{V}{\log b/a};$$

therefore

$$\int_a^b r\,dr = \frac{k_1 V}{\log b/a} \int_0^{T_1} dt,$$

where T_1 is the time which a positive ion would take to travel from a to b, *i.e.*, the time between the two discontinuities P and R.

Thus

$$\frac{b^2-a^2}{2} = k_1 \frac{V}{\log b/a} \cdot T_1,$$

i.e.,

$$k_1 = \tfrac{1}{2}(b^2-a^2) \log \frac{b}{a} \cdot \frac{1}{VT_1}.$$

Similarly, for the negative ion,

$$k_2 = \tfrac{1}{2}(b^2-a^2) \log \frac{b}{a} \cdot \frac{1}{VT_2},$$

T_2 being the time between the two discontinuities P and Q.

In this experiment the inside diameter of the outer cylinder is 4·1 cm., and the outside diameter of the inner cylinder is 1·1 cm.

$\frac{1}{2}(b^2-a^2) \log b/a$ is therefore equal to $\frac{1}{2}(4{\cdot}1^2-1{\cdot}1^2) \log_e \left(\frac{4{\cdot}1}{1{\cdot}1}\right) = 2{\cdot}56.$

Therefore

$$k_1 = \frac{2{\cdot}56}{VT_1}, \qquad k_2 = \frac{2{\cdot}56}{VT_2}.$$

Several different forms of ionisation vessel were tried before one was

found which worked satisfactorily when immersed in liquid air. In several forms the strain on the ebonite insulation which was caused by the unequal contraction of ebonite and brass was sufficient to break the dielectric, while in another form this unequal contraction made the vessel leak and so liquid air made its entrance.

The form of vessel shown in longitudinal section in fig. 6, however, worked quite satisfactorily. V is a cylindrical brass vessel which contains the two brass electrodes A and B.

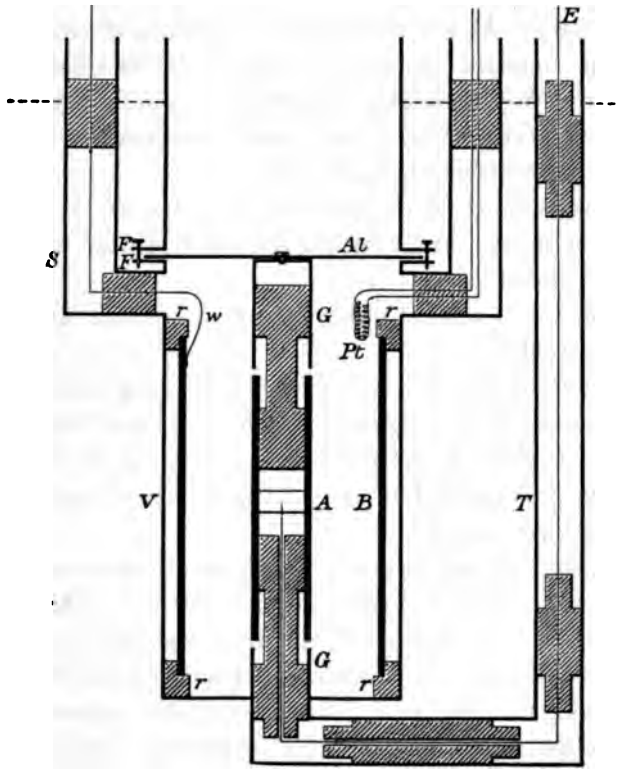


FIG. 6.

B is very little smaller than the vessel and is kept in position and insulated from it by means of ebonite rings at the top and bottom which are shown in section at *r*, *r*.

It is connected with the point *b* (fig. 5) by means of the wire *w* which is led out through ebonite plugs in the side tube S.

Through the centre of bottom of the vessel is soldered the lower guard tube G, while the upper guard tube is screwed to the centre of the aluminium lid Al.

The electrode A is supported between these two guard rings by means of ebonite plugs which are shown in section shaded, and it is connected to one of the mercury cups M (fig. 5) by means of a wire led out through the tube T.

The ebonite plugs are turned as shown in order to increase the insulating surface and so improve the insulation.

Pt is a platinum resistance which takes up very little space and which serves to measure the temperature of the air between the electrodes. The leads to this are led out through ebonite plugs in another side tube.

The aluminium lid Al fits into a depression which is turned in the lower flange F and is squeezed by screws between the two flanges F, F. The ebonite plugs are very close fitting so that the vessel is very nearly air-tight and a P_2O_5 drying tube, which is not shown, communicates with the interior of the vessel by means of another side tube.

The whole vessel and side tubes can be contained in a beaker 8 cm. diameter so that it may easily be immersed in liquid air up to the position indicated by the dotted line.

The Röntgen bulb is vertically above the vessel so that rays enter through the aluminium lid Al.

The standard vessel is of much simpler design, being merely a brass vessel with an aluminium window through which rays enter between two plane electrodes, one of which is connected to one end of the 160-volt battery, while the other is connected to one of the mercury cups M in fig. 5. A single reading is taken as follows:—

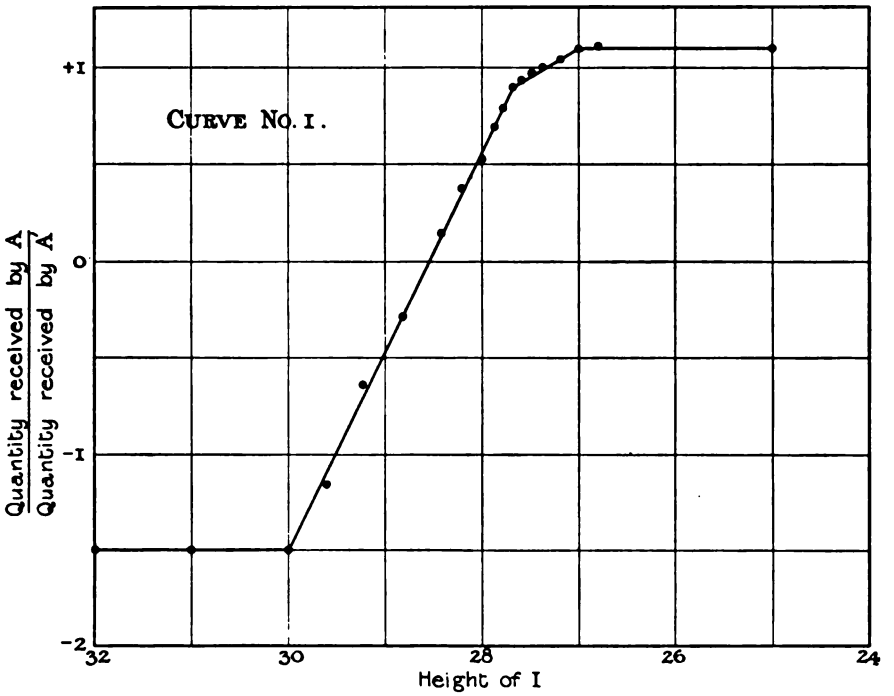
First I is placed at the required height on the scale and the contact is made. A, A′ and the electrometer are all earthed. The electro-magnet circuit is closed and the weights W and W′ are placed in position. A and A′ are insulated. The contact I′ is made and then the electro-magnet circuit is broken, allowing the weights to fall and break the contacts I and I′. The contact I is re-made and the quantities received by A and A′ are measured successively on the electrometer. The ratio of these two quantities is plotted against the scale reading of I.

A typical series at 12° C. is given on p. 173.

Plotting these quantities against each other we obtain Curve No. 1, from which we see that the points P, Q, and R occur at the scale readings 30 cm., 27·7 cm., and 27·0 cm., respectively.

Potential of cells = 80 volts.

Scale reading of I.	Quantity received by A / Quantity received by A′	Scale reading of I.	Quantity received by A / Quantity received by A′
32·0	−1·5	27·8	+0·80
31·0	−1·5	27·7	+0·90
30·0	−1·5	27·6	+0·94
29·6	−1·15	27·5	+0·98
29·2	−0·73	27·4	+1·00
28·8	−0·28	27·2	+1·04
28·4	+0·15	27·0	+1·10
28·2	+0·37	26·8	+1·10
28·0	+0·55	25·0	+1·10
27·9	+0·70		



When the contact breaker I is placed at 30 cm. on the scale the distance between it and the electro-magnet is 11·5 cm. The height of the falling weight itself is 4·2 cm., therefore the actual height of fall of the weight before breaking the contact = 7·3 cm.

Height of fall to 27·7 cm. = 9·6 cm.

„ „ 27·0 „ = 10·3 „

The time of fall to 30·0 cm. = $\sqrt{\frac{2 \times 7{\cdot}3}{981}}$ sec. = 0·1220 sec.

The time of fall to 27·7 cm. $= \sqrt{\frac{2 \times 9{\cdot}6}{981}}$ sec. $= 0{\cdot}1400$ sec.

„ 27·0 „ $= \sqrt{\frac{2 \times 10{\cdot}3}{981}}$ sec. $= 0{\cdot}1450$ sec.

Therefore The time from P to Q $= 0{\cdot}0180$ sec.

and „ „ P to R $= 0{\cdot}0230$ „

$$k_1 = \frac{2{\cdot}56}{0{\cdot}023 \times 80} = 1{\cdot}39 \text{ cm./sec. per volt/cm.}$$

$$k_2 = \frac{2{\cdot}56}{0{\cdot}018 \times 80} = 1{\cdot}78 \quad \text{„} \quad \text{„}$$

The results at ordinary temperatures show that the apparatus is working satisfactorily.

The following is a typical set of readings taken when the apparatus is immersed in liquid air up to the position indicated by the dotted lines in fig. 6.

Potential of cells = 82 volts. Resistance of Pt thermometer steady at 0·90 ohm.

Scale reading of I.	$\frac{\text{Quantity received by A}}{\text{Quantity received by A}'}$	Scale reading of I.	$\frac{\text{Quantity received by A}}{\text{Quantity received by A}'}$
32·0	−1·67	21·0	+0·162
30·0	−1·67	17·0	+0·60
29·3	−1·36	13·0	+1·01
28·34	−1·09	9·0	+1·36
27·82	−0·933	5·0	+1·60
26·8	−0·72	1·0	+1·60
25·0	−0·39	−5·0	+1·60
23·0	−0·10		

These numbers are plotted in Curve No. 2, which only shows two points of discontinuous curvature, the one occurring at the scale-reading 30 cm., the other at 5·5 cm.

This would lead us to the conclusion that the velocities of the positive and negative ions are equal to one another.

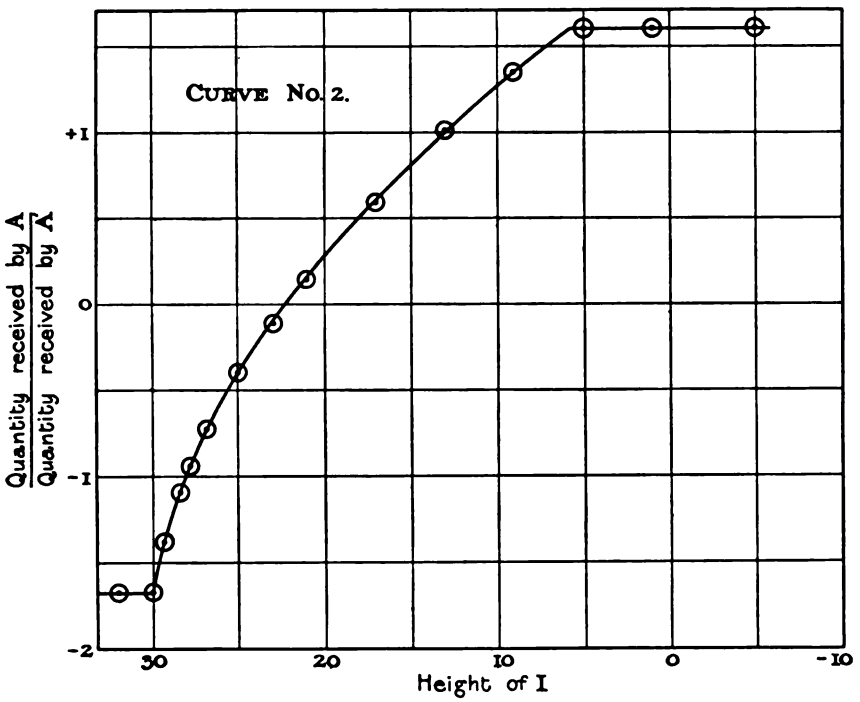
Time to fall to 30 cm. $= 0{\cdot}1220$ sec.

„ „ 5·5 „ $= \frac{2 \times 31{\cdot}8}{981} = 0{\cdot}2546$ sec.

Thus Time between discontinuities $= 0{\cdot}1346$ sec.,

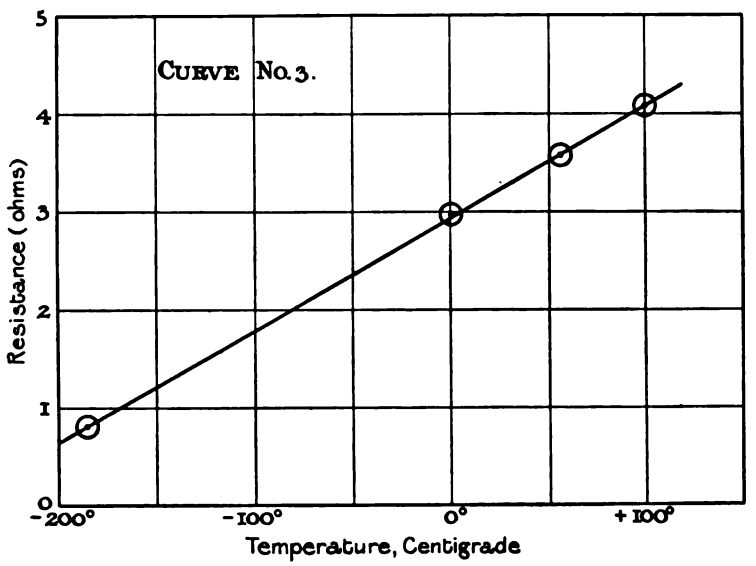
i.e., k_1 and $k_2 = \frac{2{\cdot}56}{82 \times 0{\cdot}1346} = 0{\cdot}232$ cm./sec. per volt/cm.

To calibrate the platinum thermometer its resistance was found when



it was immersed in freshly prepared liquid air (−186° C.), water at 0° C., water at 57° C., and water at 100° C.

The calibration curve is given in Curve No. 3, which shows that when the resistance is 0·90 ohm the temperature is −180° C.



Temperature.	Resistance.
° C.	ohms.
−186	0·82
0	2·97
57	3·57
100	4·03

The disappearance of the one point of discontinuous curvature might be due to some defect in the apparatus; such a defect, for instance, as would arise from the difference of coefficient of expansion of ebonite and brass. This might conceivably allow the central electrode to get a little out of the centre, and this would very soon round off any corners in the curve. After taking several precautions to prevent such an occurrence, however, the other point does not reappear, and if we examine the curve, the sharpness of the other discontinuities seems to show that there is no such defect.

Five series of readings were obtained with the vessel immersed in liquid air, and the curves obtained were exactly similar. The velocities found were:—

Velocity.	Temperature.
cm./sec. volt/cm.	° C.
0·232	−180
0·237	−179
0·239	−177
0·234	−180
0·235	−179
Mean 0·235	−179

i.e., at −179° C. the velocities of the positive and negative ions are each equal to 0·235 cm./sec. per volt/cm.

Determination of the Velocities at −65° C.—In this experiment the ionisation vessel consists of a double-walled metal jacket, inside which the electrodes are contained, and the space between the walls of which is filled with solid CO_2.

A diagram of the vessel is given in fig. 7.

In order to keep the space between the double walls filled with solid CO_2, liquid CO_2 is allowed to escape from a cylinder through a small hole. It enters the jacket through the tube E, which is screwed into the cylinder, and the gas is led out through the tubes L and allowed to escape outside the window.

Unfortunately a steady stream of CO_2 cannot be maintained in this way, for the small hole gets choked with the solid and so one cannot merely leave the stream flowing, but by keeping an eye on the temperature and blowing more CO_2 through when it shows signs of falling, it is quite easily maintained between the limits $-62°$ and $-68°$ C. The vessel was surrounded with three layers of thick felt in order to protect it from being warmed up too rapidly by external radiation.

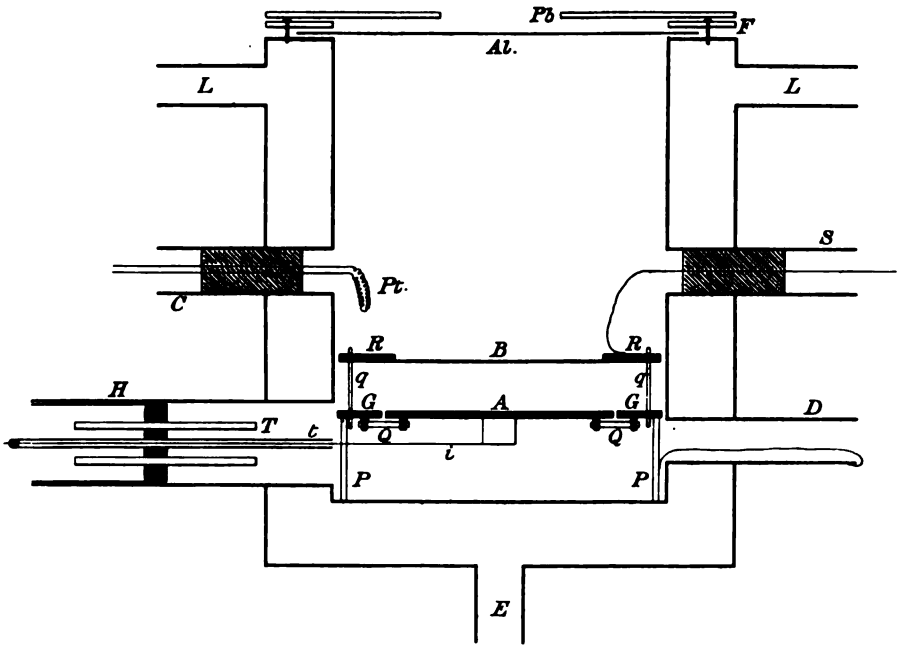


FIG. 7.

The electrode A is of thick brass, and is insulated from the guard ring G by means of three rods of quartz Q, whose ends are soldered to G and A respectively. The guard ring is supported by three brass pillars P, which are soldered to it and which rest on the base of the vessel.

The electrode B is of aluminium and is screwed to the brass ring R. It is supported by three quartz rods *q*, which are soldered into holes in G and R. Three spacing blocks, 0·96 cm. thick, were placed between A and B while the quartz rods *q* were being soldered, and thus the electrodes were fixed accurately parallel. The wire connecting B with the point *b* in fig. 5 is led out through an ebonite plug in the side tube S.

The wire *i* connecting A to a mercury cup (M in fig. 5) is threaded through a narrow brass tube *t*. This is soldered into the quartz tube T, which in its turn is soldered into a wider brass tube. This brass tube

slides tightly into the side tube H, making a fairly air-tight joint. The wire *i* is pulled taut, and is then soldered to the outer end of *t*.

The leads to the platinum thermometer Pt are led in through an ebonite plug in the side tube C.

The side tube D serves a double purpose. A P_2O_5 drying tube is attached to it, and through it a wire which is soldered to the guard ring is led out and soldered into good contact with the vessel.

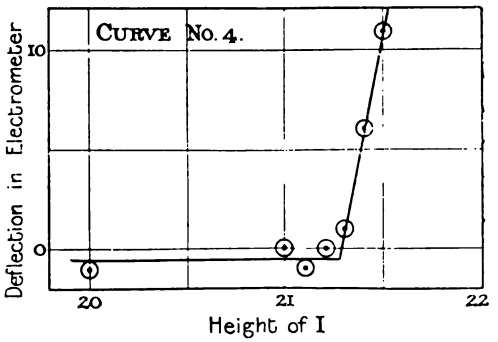
The lid of the vessel Al is of thin aluminium and is made fairly air-tight by being squeezed between a brass ring F and the top of the double-walled jacket. A lead shield Pb only allows the rays to impinge centrally on the electrodes.

Since the rays impinge directly on the brass electrode A, the secondary radiation makes the ionisation very intense close to A, so that in this case the null method is applied. The method of taking a reading is exactly the same as described for the temperature, −179° C., except that the two electrodes A and A′ are connected together all the time instead of being connected separately to the electrometer. A typical series of readings is given below :—

Potential of cells = 85 volts. Electrode B is negative before reversal.

Scale reading of I.	Deflection in electrometer.
cm.	mm.
20·0	− 1
21·0	0
21·1	− 1
21·2	0
21·3	+ 1
21·4	+ 6
21·5	+11

These numbers are plotted in Curve No. 4 which shows that the point of discontinuity R is at 21·28 cm.



The resistance of the platinum thermometer never varied beyond the limits 2·31 and 2·25 ohms. Exactly similar series of readings were conducted to find the points P and Q.

The point P is at 25·25 cm. scale reading, and
„ Q „ 22·22 „ „
Now the height of fall to 25·25 cm. = 59·70 cm.
„ „ 21·28 „ = 63·67 „
„ „ 22·22 „ = 62·73 „

Thus

$$\text{Time of fall to } 25{\cdot}25 = \sqrt{\frac{119{\cdot}4}{981}} = 0{\cdot}3490 \text{ sec.}$$

$$\text{„ „ } 21{\cdot}28 = \sqrt{\frac{127{\cdot}34}{981}} = 0{\cdot}3606 \text{ sec.}$$

$$\text{„ „ } 22{\cdot}22 = \sqrt{\frac{125{\cdot}46}{981}} = 0{\cdot}3580 \text{ sec.}$$

Thus

Time between P and Q = 0·0090 sec.,

and „ P and R = 0·0116 „

Now distance between electrodes = 0·96 cm., and potential on electrodes = 0·85 volt. Thus

$$k_1 = \frac{0{\cdot}96}{0{\cdot}0116} \times \frac{0{\cdot}96}{85} = 0{\cdot}935 \text{ cm./sec. per volt/cm.}$$

$$k_2 = \frac{0{\cdot}96}{0{\cdot}0090} \times \frac{0{\cdot}96}{85} = 1{\cdot}21 \quad \text{„ „}$$

Inspecting the Pt thermometer calibration curve, we see that the temperature is between −62° and −68° C. The mean temperature is thus −65° C.

Owing to the large amount of CO_2 which was required to keep the temperature constant, only three series of readings could be taken before the cylinder of liquid CO_2 was exhausted. The results of these three series are:—

	k_1.	k_2.	Temperature Limits.	Mean Temperature.
			°C.	°C.
	0·935	1·21	−62 to −68	−65·0
	0·95	1·25	−60 to −65	−62·5
	0·95	1·22	−61 to −66	−63·5
Mean	0·945	1·23	—	−63·7

Determinations of the velocities at temperatures 12° *C. to* 138° *C.*—These determinations have been made with two different forms of ionisation vessel. The first form of ionisation vessel is the same as that used for −65°.

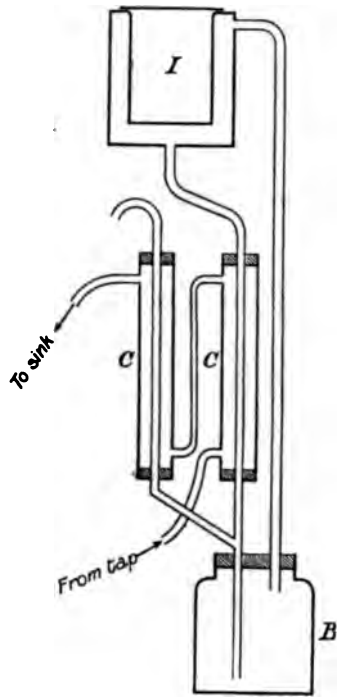


Fig. 8.

A boiler and two condensers were fitted up as in fig. 8 so that a rapid stream of vapour could be driven through the jacket in fig. 7 and condensed back again into the boiler. B is the boiler, C, C are two condensers and I is the double-walled ionisation vessel. Three different liquids were used in B, methylated spirits, water and amyl alcohol, giving temperatures of 75°, 100° and 126° respectively.

Exactly the same operations were gone through in this case as were gone through in the determinations at −65° C. A null method was used and the points P, Q, and R found by travelling along the horizontal parts of the curves until a deflection was obtained.

A number of determinations were made at the ordinary temperature of the room and the following values of k_1 and k_2 were obtained :—

k_1.	k_2.	Temperature.
		°C.
1·38	1·77	12
1·39	1·77	11
1·41	1·80	12
1·37	1·78	11
1·41	1·81	14
Mean 1·39	1·79	12

Probably the most accurate determinations so far are those of Langevin and Zeleny. Their results are :—

	k_1.	k_2.
Langevin.....	1·40	1·70
Zeleny.....	1·36	1·87

We may, therefore, conclude that the apparatus is working quite satisfactorily.

The series of experiments with the jacket heated to 75° C. by means of methylated spirits gave the following results:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
	cm.	cm.	sec.	sec.	volts.	
1	25·25	59·70	0·3490			
	22·89	62·06	0·3557	0·0067	81	1·69
	23·38	61·57	0·3543	0·0053	—	2·14
2	25·25	59·70	0·3490			
	22·95	62·00	0·3555	0·0065	—	1·67
	23·43	61·52	0·3541	0·0051	85	2·12
3	25·25	59·70	0·3490			
	22·85	62·10	0·3558	0·0068	80	1·69
	23·33	61·62	0·3544	0·0054	—	2·13
4	25·25	59·70	0·3490			
	22·90	62·05	0·3557	0·0067	84	1·62
	23·40	61·55	0·3542	0·0052	—	2·11

From these experiments we have:—

	k_1.	k_2.	Temperature.
			° C.
	1·69	2·14	+75
	1·67	2·12	
	1·69	2·13	
	1·62	2·11	
Mean	1·67	2·125	+75

With the boiler filled with water, *i.e.*, with the vessel maintained at 100° C., the following results were obtained:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 25·25	cm. 59·70	sec. 0·3490	sec.	volts.	
1	22·99	61·96	0·3554	0·0064	80	1·80
	23·44	61·51	0·3541	0·0051	—	2·26
2	23·15	61·80	0·3550	0·0060	85	1·81
	23·52	61·43	0·3539	0·0049	—	2·21
3	23·15	61·80	0·3550	0·0060	83	1·85
	23·48	61·47	0·3540	0·0050	—	2·22
4	22·99	61·96	0·3554	0·0064	82	1·76
	23·41	61·54	0·3542	0·0052	—	2·16
5	23·15	61·80	0·3550	0·0060	84	1·83
	23·48	61·47	0·3540	0·0050	—	2·19

Thus we have at 100° C.:—

k_1.	k_2.
1·80	2·26
1·81	2·21
1·85	2·22
1·76	2·16
1·83	2·19
Mean 1·81	2·21 cm./sec. per volt/cm.

With the boiler filled with amyl alcohol, *i.e.*, with the vessel at a temperature of 126° C., the following results were obtained:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 25·25	cm. 59·70	sec. 0·3490	sec.	volts.	
1	23·34	61·61	0·3544	0·0054	89	1·91
	23·69	61·26	0·3534	0·0044	—	2·36
2	23·24	61·71	0·3547	0·0057	82	1·97
	23·62	61·33	0·3536	0·0046	—	2·44
3	23·31	61·64	0·3545	0·0055	85	1·97
	23·66	61·29	0·3535	0·0045	—	2·41
4	23·15	61·80	0·3550	0·0060	80	1·92
	23·52	61·43	0·3539	0·0049	—	2·36
5	23·31	61·64	0·3545	0·0055	84	1·99
	23·66	61·29	0·3535	0·0045	—	2·43

Thus we have at +126° C.:—

k_1.	k_2.
1·91	2·36
1·97	2·44
1·97	2·41
1·92	2·36
1·99	2·43
Mean 1·95	2·40 cm./sec. per volt/cm.

The velocities of the ions at 13°, 60°, 110° and 138° were also found by means of another ionisation vessel. It is shown in section in fig. 9.

The vessel itself, V, is a brass casting of which the inside dimensions are about 4 × 4 × 2 inches. A and B are two brass electrodes and G is a guard ring. A and B are fixed in position by being screwed to brass rods which are soldered into quartz tubes Q, Q, while these in their turn are soldered into the cups C, C, which are turned in the sides of the vessel. While the solder is being poured into the cups the two electrodes are fixed parallel and 0·96 cm. apart by means of three spacing blocks.

The two tubes S and T fit on to the outside of the cups, and are soldered in position. Through them the connections to B and A are made by means

of the two brass rods E, H, which screw into little blocks on the ends of *r*, *r*.

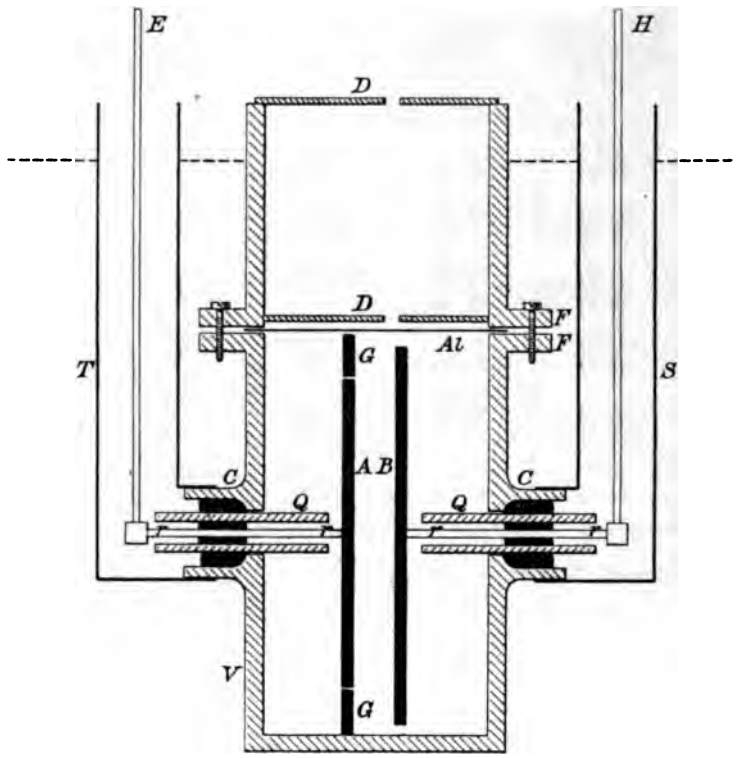


Fig. 9.

Al is the aluminium lid to the vessel and is made tight by being squeezed between the two flanges F, F.

D, D are two brass diaphragms which only allow a flat pencil of rays about 3 mm. thick to enter the vessel, and which are so placed that this pencil just grazes the surface of B. There is a continuation of the vessel above the aluminium lid so that the whole may be immersed in an oil bath up to about the position indicated by the dotted lines.

The oil bath can be maintained at any constant temperature between about 30° and 150° by means of a thermostat.

The mode of using this vessel was exactly the same as in the last experiments. A null method was used and the height of the movable contact breaker I varied, to find the point at which one begins to get a permanent deflection. With this apparatus the point was very sharply marked.

The following results were obtained when the vessel was at the temperature of the laboratory :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 29·35	cm. 56·72	sec. 0·3400	sec.	volts.	
1. 12° C.	26·69	59·38	0·3479	0·0079	84	1·39
	27·27	58·80	0·3462	0·0062	—	1·77
2. 13° C.	26·83	59·24	0·3475	0·0075	88	1·40
	27·37	58·70	0·3459	0·0059	—	1·77
3. 11° C.	26·52	59·55	0·3484	0·0084	80	1·37
	27·16	58·91	0·3466	0·0066	—	1·75
4. 15° C.	26·71	59·36	0·3478	0·0078	83	1·42
	27·30	58·77	0·3461	0·0061	—	1·82

Thus we have :—

k_1.	k_2.	Temperature.
		° C.
1·39	1·77	12
1·40	1·77	13
1·37	1·75	11
1·42	1·82	15
Mean 1·395	1·78	13

The following results were obtained with the oil bath maintained at 60° C. :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 29·35	cm. 56·72	sec. 0·3400	sec.	volts.	
1	27·07	59·00	0·3468	0·0068	84	1·61
	27·51	58·56	0·3455	0·0055	—	1·99
2	27·05	59·02	0·3469	0·0069	84	1·59
	27·53	58·54	0·3454	0·0054	—	2·03
3	27·15	58·92	0·3466	0·0066	86	1·62
	27·59	58·48	0·3453	0·0053	—	2·02
4	26·92	59·15	0·3473	0·0073	80	1·58
	27·39	58·68	0·3459	0·0059	—	1·95

Thus we have at 60° C. :—

k_1.	k_2.
1·61	1·99
1·59	2·03
1·62	2·02
1·58	1·95
Mean 1·60	2·00 cm./sec. per volt/cm.

With the oil bath maintained at 110° C. the following results were obtained :—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 29·35	cm. 56·72	sec. 0·3400	sec.	volts.	
1	27·37	58·70	0·3459	0·0059	84	1·86
	27·77	58·32	0·3448	0·0048	—	2·28
2	27·23	58·84	0·3464	0·0064	80	1·80
	27·67	58·40	0·3450	0·0050	—	2·30
3	27·29	58·78	0·3462	0·0062	80	1·85
	27·70	58·37	0·3449	0·0049	—	2·35
4	27·40	58·67	0·3459	0·0059	83	1·88
	27·70	58·37	0·3449	0·0049	—	2·26

Thus we have :—

k_1.	k_2.
1·86	2·28
1·80	2·30
1·85	2·35
1·88	2·26
Mean 1·85	2·30 cm./sec. per volt/cm. at 110° C.

With the oil bath maintained at 138° C. the following results were obtained:—

Experiment.	Scale reading of the points P, Q, R.	Height of fall to these points.	Time of fall.	Time between P and Q and P and R.	Potential.	k.
All expts. P at	cm. 29·35	cm. 56·72	sec. 0·3400	sec.	volts.	
1	27·53	58·54	0·3454	0·0054	85	2·00
	27·89	58·18	0·3443	0·0043	—	2·52
2	27·49	58·58	0·3456	0·0056	84	1·96
	27·86	58·21	0·3445	0·0045	—	2·44
3	27·53	58·54	0·3455	0·0055	84	1·99
	27·89	58·18	0·3444	0·0044	—	2·49
4	27·58	58·49	0·3453	0·0053	85	2·05
	27·92	58·15	0·3443	0·0043	—	2·53

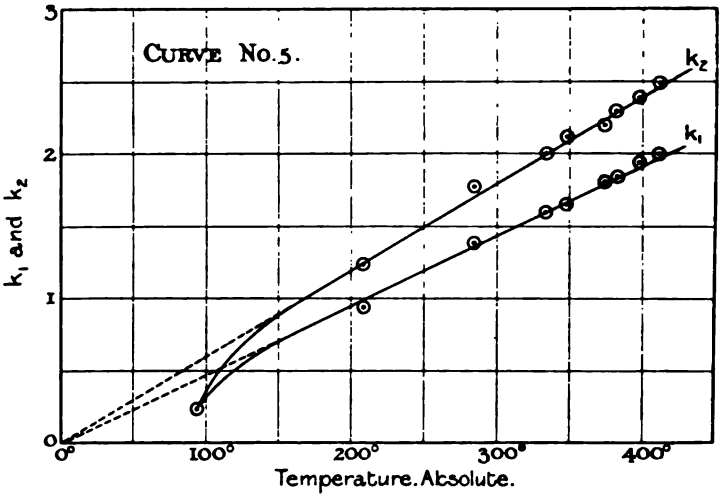
Thus we have:—

k_1.	k_2.
2·00	2·52
1·96	2·44
1·99	2·49
2·05	2·53
Mean 2·00	2·495 cm./sec. per volt/cm. at 138° C.

Collecting all the results at the different temperatures we get:—

k_1.	k_2.	Temperature absolute.
		° C.
2·00	2·495	411
1·95	2·40	399
1·85	2·30	383
1·81	2·21	373
1·67	2·125	348
1·60	2·00	333
1·39	1·785	285
0·945	1·23	209
0·235	0·235	94

These numbers are plotted in Curve No. 5.



We see that except for the case of the velocities at 94° abs. the points lie very close to straight lines through the origin, *i.e.*, k_1 and k_2 are very nearly proportional to the absolute temperature. This is a strangely simple result when we consider what a complication of circumstances affects the velocities.

Interpretation of the Results.—As is well known, by making use of the kinetic theory of gases, we can obtain an expression for the drift velocity U of an ion in an electric field in the form

$$U = \tfrac{1}{2} \frac{e}{m_2} \frac{\lambda_2}{v_2} X,$$

where X is the field,

m_2 is the mass of the ion,

λ_2 is the mean free path of the ion, and

v_2 is the mean molecular velocity of the ion.

This formula depends upon the fundamental assumptions—

1. That statically the previous history of the ion is wiped out at each collision.
2. That the drift velocity is small compared with the mean molecular velocity. This condition is easily fulfilled.

It is easy to see that the first assumption is correct if the ions consist of one molecule each, but it is probably not quite accurate when they consist of more than one. It is difficult, however, to make any other workable assumption and, if we make it, it is fairly simple to find U in terms of m_1, λ_1, v_1 (the corresponding quantities for the gas molecules), and n, the number of molecules which go to make up one ion.

For let N_1 be the number of molecules per cubic centimetre, and

N_2 „ „ ions „ „

Let r_1 be the radius of a molecule, and r_2 of an ion $= n^{\frac{1}{3}}r$,

$2r_{12}$ = distance between centres of a molecule and an ion at a collision $= (r_1+r_2)$,

$v_2 = v_1/\sqrt{r}$.

Then, treating the mixture of ions and molecules as a mixture of two different gases, the mean free path, λ_2, of an ion is given by

$$\lambda_2^{-1} = \pi\left[N_2 r_2^2\left(1+\frac{m_2}{m_2}\right)^{\frac{1}{2}} + N_1 r_{12}^2\left(1+\frac{m_2}{m_1}\right)^{\frac{1}{2}}\right].*$$

Now N_2 is negligible compared with N_1; thus

$$\lambda_2^{-1} = \Pi N_1 r_{12}^2(1+n)^{\frac{1}{2}} = \tfrac{1}{4}\Pi N_1 r_1^2(1+n^{\frac{1}{3}})^2(1+n)^{\frac{1}{2}}$$
$$= \tfrac{1}{8}\sqrt{2}\,\lambda_1(1+n^{\frac{1}{3}})^2(1+n)^{\frac{1}{2}}.$$

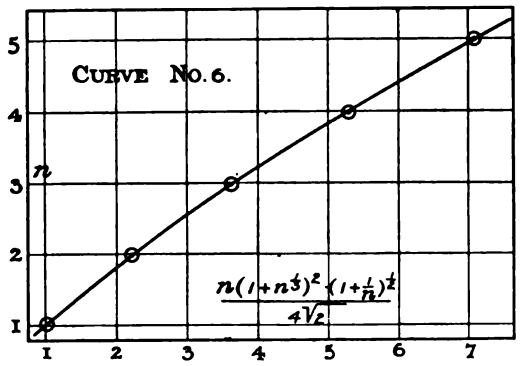
Thus

$$\frac{e}{m_2}\frac{\lambda_2}{v_2} = \left[\frac{4\sqrt{2}}{n(1+n^{\frac{1}{3}})^2\left(1+\frac{1}{n}\right)^{\frac{1}{2}}}\right]\frac{e}{m_1}\frac{\lambda_1}{v_1}.$$

The factor in the brackets is too complex for one to see at a glance how it varies with n. The following are the values of its inverse when $n = 1, 2, 3, 4$, and 5:—

$n = 1$	1
2	2·21
3	3·65
4	5·31
5	7·12

These are plotted in Curve No. 6.



Now the value of $\frac{1}{2}\frac{e}{m_1}\frac{\lambda_1}{v_1}$ for air at 76 cm. pressure and 0° C. is equal to 770, when we use the values for the size of the molecules given in Jeans'

* Jeans, 'Dyn. Theory of Gases,' p. 234.

'Dyn. Theory of Gases,' p. 340, the number of molecules per cubic centimetre given by the electrical methods of J. J. Thomson and H. A. Wilson, and the electrolytic values of e/m. These, I think, are the most reliable values we can get.

The velocity of the positive ion given by Curve 5 is about 1·33 cm./sec. per volt/cm., *i.e.*, 399 cm./sec. per absolute unit of field, at 0° C.

This is 1·93 times too small, therefore

$$\frac{n(1+n^{\frac{1}{3}})^2\left(1+\frac{1}{n}\right)^{\frac{1}{2}}}{4\sqrt{2}} = 1{\cdot}93.$$

From Curve 6 we see that this would require n to be about 1·8. That is at 0° C. and 76 cm. pressure a positive ion in air consists on an average of 1·8 molecules.

M. Langevin* found it necessary, in order to explain the slowness of diffusion of the ions, to assign to them a size twice or thrice the size of a molecule, while Dr. Richardson,† from considerations based on the variation of the ionic velocities with pressure, came to the conclusion that a positive ion in air at atmospheric pressure and at ordinary temperatures consists of about 3 molecules.

By making the same calculation as the above from the experimental results at different temperatures, we get the variation with temperature of the number of molecules in the ion. The calculated values of n are given in the following table:—

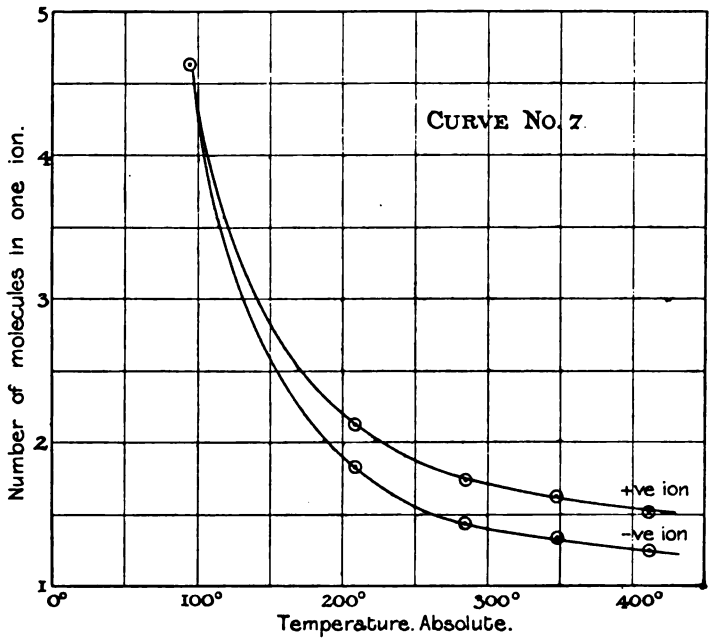
Temperature absolute.	n (positive).	n (negative).
° C.		
94	4·63	4·63
209	2·12	1·82
285	1·76	1·43
348	1·64	1·34
411	1·52	1·25

These numbers are plotted in Curve No. 7.

Of course, the first assumption made in deducing the formula $\frac{1}{2} \times \frac{e}{m}\frac{\lambda}{v}$ will show us that we cannot accurately deduce the number of molecules in an ion in this way. Probably all the numbers have to be multiplied by a factor which is not very far different from unity, but at least this curve will show us how the size of the ion varies with the temperature.

* 'Comptes Rendus,' vol. 111, p. 35, 1905.

† 'Phil. Mag.,' July, 1905.



The fact that it varies continuously and not in jumps would seem to show that there is a continual exchange going on between ions and uncharged molecules; at some collisions several molecules remain attached to the ion, while at others one or more of them is knocked off, and so a dynamical equilibrium is set up.

As the temperature of the gas rises, the collisions are more violent, and statistically fewer molecules are attached to an ion; this gradual change would go on until the collisions become so violent that at times corpuscles are shot off without even a single molecule attached to them. When this happens the velocity of the ion would very rapidly increase with the temperature, and so in flames we might expect those rapidly moving ions which are unloaded corpuscles for an appreciable fraction of their life.

In conclusion, I wish to express my indebtedness to Professor J. J. Thomson for suggesting this subject for investigation and for the kindly interest he has shown while the experiments have been in progress. I also wish to thank Dr. Richardson for some helpful suggestions.

The Ionisation Produced by Hot Platinum in Different Gases.

By O. W. RICHARDSON, M.A., Fellow of Trinity College, Cambridge, Clerk-Maxwell Student.

(Communicated by Professor J. J. Thomson, F.R.S. Received June 19,—Read June 28, 1906.)

(Abstract.)

The primary object of this investigation has been to try to discover the mechanism of the action by which the positive ions set free by hot bodies originate. It deals principally with measurements of the *steady* positive ionisation produced by hot platinum in various gases under different conditions.

In 1901* the writer showed that the negative ionisation from hot metals could be satisfactorily explained by supposing that it was caused by the freely moving corpuscles inside the metal escaping from the surface when their kinetic energy exceeded a certain value. In the present paper reasons are assigned for believing that a view of this kind will not account for the origin of the positive ions, which seem to be liberated by an action in which the atoms of the gas play a direct part. In the cases of steady ionisation here investigated it seems probable that it is not so much the external gas as that adsorbed by the metal which is effective.

It has been known for a long time that when a wire is heated for the first time it furnishes a very copious emission of positive ions. This effect has been examined previously in some detail by the writer,† who showed that it was very noticeable in a good vacuum and that the ionisation decayed asymptotically with time to a very small value. More recently the writer‡ has succeeded in showing that the reduced value of the leak thus obtained could be increased by the admission of small quantities of air. Further investigation has shown that there is a portion of the positive ionisation which is a function of the pressure of the external gas. It is with this part of the ionisation that the present paper chiefly deals.

Although the ionisation of this type is well marked and definite, its value even at atmospheric pressure is small compared with the initial value of the leak from a new wire.

The experimental methods employed are similar to those previously made

* 'Camb. Phil. Soc. Proc.,' vol. 11, p. 286 ; *cf.* also 'Phil. Trans.,' A, vol. 201, p. 473.

† 'Phil. Mag.' [6], vol. 6, p. 80.

‡ 'Camb. Phil. Soc. Proc.,' vol. 13, p. 58.

use of by the writer. Any important deviations from earlier methods are described in the paper. The investigation is more complete in the case of oxygen than of the other gases investigated, because: (1) oxygen was found to have a considerably greater effect on the ionisation, especially at low pressures; and (2) it is a simple elementary gas, which is easily prepared in a state of considerable purity.

Besides oxygen the paper contains an account of measurements of the ionisation of both signs from hot platinum in air, nitrogen, helium, and hydrogen. There are also measurements of the ionisation from a platinum surface in air when a calculable quantity of hydrogen is diffusing out from the interior of the platinum. The last-named experiments shed a considerable amount of light on the mechanism of the processes by which both the positive and negative ions are produced.

It has been found convenient to subdivide the paper according to the following scheme:—

I. § 1. Introduction.
II. § 2. Experimental Arrangements.
III. The Ionisation in Oxygen:—
§ 3. Current and Electromotive Force.
§ 4. Hysteretic Relations between Current and Electromotive Force.
§ 5. Current and Pressure.
§ 6. Current and Temperature.
§ 7. Uncontrollable Variations.
§ 8. Comparison of different Wires.
§ 9. Special Properties of New Wires.
§ 10. Theory of the Steady Positive Leak in Oxygen.
IV. § 11. The Ionisation in Nitrogen.
V. § 12. The Ionisation in Air.
VI. § 13. The Ionisation in Helium.
VII. § 14. The Ionisation in Hydrogen.
VIII. § 15. Experiments with a Platinum Tube.
IX. § 16. Theoretical Considerations.
X. § 17. Summary of Principal Results.

The following is a brief account of the chief results of the investigation:—

The positive ionisation, *i.e.*, the number of positive ions produced by 1 sq. cm. of platinum surface per second, possesses a minimum value, which depends on temperature and pressure, in most gases. The positive ionisation in oxygen at a low pressure (less than 1 mm.) is much greater than in the other gases tried. In oxygen, at low pressures and temperatures below 1000° C., the ionisation varies as the square root of the pressure; at higher

temperatures and low pressures it varies nearly directly as the pressure; whilst at higher pressures at all temperatures the variation with pressure is slower, so that at pressures approaching atmospheric the ionisation becomes practically independent of the pressure.

The variation with pressure in air is similar to that in oxygen. In nitrogen and hydrogen the ionisation appeared to increase more rapidly with the pressure at high pressures than in oxygen. In very pure helium at low pressures there was a positive ionisation which was a function of the pressure.

The experiments on ionisation by collisions indicate that the positive ions liberated by hot platinum in oxygen are of the same order of magnitude as those set free by the collisions. They are not great masses approximating to dust particles.

The positive leak in oxygen always oscillated around a certain value under specified conditions. It was, therefore, never steady, so the minimum values were taken. This variability was much less marked, if it occurred at all, in the other gases.

The minimum value of the positive ionisation was found to remain practically constant with a wire heated during three months at various times (for 150 hours altogether) in oxygen at 900°—1000° C. Moreover, four different wires of different dimensions after continued heating in oxygen gave nearly the same value for the ionisation at the same temperatures and pressures.

The positive ionisation in air at constant temperature is smaller than that which would be obtained if the nitrogen were withdrawn, so as to leave only oxygen at a low pressure. The nitrogen, therefore, exerts an inhibiting effect on the oxygen.

The minimum value of the positive ionisation at a definite pressure in all gases appears to be connected with the temperature by the relation first deduced by the author for the negative ionisation. This relation may be written $i = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, where i is the ionisation, θ is the absolute temperature and A and Q are constants. The value of the constant Q, which is a measure of the energy associated with the liberation of an ion, is in most cases smaller for the positive than for the negative ionisation.

These results refer to wires which have been heated in a vacuum, and subsequently in the gas considered, for a long time. New wires exhibit peculiar properties, especially in regard to their behaviour under different electromotive forces. Old wires also exhibit hysteretic effects with change of pressure.

The view is developed that the positive ionisation is caused by the gas

adsorbed by the metal and the consequence examined of supposing the ionisation to be proportional to the amount of the adsorbed gas present. In the case of oxygen, by making the assumption that the rate of increase of the amount of the adsorbed gas is proportional jointly to the concentration of the external dissociated oxygen and to the area of "unoccupied" platinum surface, whilst the rate of breaking up is proportional to the amount present, a formula is obtained which agrees with the experimental results. This formula is that the ionisation $i = Ap/(B+p)$, where $p = (kP + \frac{1}{4}k^2)^{\frac{1}{2}} - \frac{1}{2}k$, P being the external pressure and k the dissociation constant of oxygen; A, B and k are constants depending on the temperature and are of the general form $a\theta^b e^{-b/\theta}$. Thus this view accounts for both the temperature and pressure variation.

The positive ionisation from the outer surface of a hot platinum tube in air is increased when hydrogen is allowed to diffuse through from inside the apparatus. The increase in the ionisation is proportional at constant temperature to the quantity of hydrogen escaping from the surface in unit time. For different temperatures the effect produced by a given quantity of hydrogen is greater the higher the temperature.

The negative ionisation from hot platinum in air is unaltered when hydrogen is allowed to diffuse out through the platinum.

These results show that neither the negative nor the positive ionisations usually observed with hot platinum heated in air or oxygen are due to residual traces of absorbed hydrogen.

Careful measurements were made to see if the negative ionisation in oxygen at low pressures varried with the pressure of the oxygen at constant temperature. Although the addition of oxygen increased the positive leak by a factor of 10, the negative leak was constant within the experimental error, in agreement with the work of previous observers.

The negative ionisation was found to have very nearly the same absolute value and the same temperature variation for two wires of different dimensions when heated in oxygen.

A wire which has been heated in hydrogen furnishes a negative ionisation which is very big compared with that from a wire heated in oxygen at the same temperature. If the hydrogen is at a pressure of the order of 1 mm. the negative ionisation can be rapidly reduced to a much smaller value by applying a high negative potential to the wire. The wire subsequently recovers its ionising power if the potential is reduced again. Under these conditions the ionisation varies in an interesting way with the time. The reduction in the ionising power of the wire appears to be caused by the bombardment of the surface by positive ions produced by collisions.

When a platinum wire, which has previously been allowed to absorb

hydrogen, is heated for a long time in a good vacuum so as to expel the gas, its ionising power does not appear to be reduced. The ionisation apparently is not a definite function of the quantity of gas absorbed by the wire. The amount of hydrogen which a platinum wire will absorb at a low pressure is much greater than is usually suspected.

The results indicate that the increase in the negative ionisation is not caused by the hydrogen directly but rather by some change it produces in the surface of the platinum.

On the Electric Inductive Capacities of Dry Paper and of Solid Cellulose.

By Albert Campbell, B.A.

(Communicated by Dr. R. T. Glazebrook, F.R.S. Received June 12,—Read June 21, 1906.)

(From the National Physical Laboratory.)

Although dry paper is widely used as a supporting and insulating material in telephone cables, the published data with regard to its specific inductive capacity (or permittivity) appear to be very meagre. For this reason Mr. Gavey, C.B., Engineer-in-Chief of the Post Office, asked us to investigate the matter, and sent for test a large number of samples of paper obtained from four different cable manufacturers. All the samples consisted of what is known as "chemical wood paper," presumably free from lignified fibre. This type of paper, according to the Society of Arts Report on the Durability of Papers, is better in lasting quality than "mechanical wood paper" or paper made from straw, jute or esparto grass. Mr. Gavey, in addition, has kindly supplied the results of some tests on actual cables and further data for some of the samples of paper. This information is embodied in Part II of the present paper.

Part I.—Tests on Dry Paper.

One of the main difficulties in the testing of paper lies in the fact that it absorbs moisture so readily; and the presence of moisture has a large effect on the specific inductive capacity and an enormous effect on the insulation-resistance. The nature of these effects is well illustrated by the curve in fig. 6 (Part II, p. 204), which shows how the capacity increases and the resistance decreases as a well-dried cable is allowed to absorb moisture from the atmosphere.

Methods of Testing.

In all cases small squares of the samples (each about 10×10 cm.) were dried in an electrically-heated oven, the mean temperature of which was kept at about 110° C. The dry paper was then made to form a part of the dielectric of a small plate condenser and the capacity of this was measured. Two distinctly different arrangements were used in forming the small condenser, and two series (A and B) of results were obtained. In the first method (A), the specimen to be tested was placed while still hot between indiarubber discs (of area 50 sq. cm.) covered with tinfoil also dry and warm. A weight of 15 kgm. was placed on the upper disc (being insulated from it) and the resulting condenser was tested as it cooled down. In method (B)* a small air condenser was formed from two well-trued circular brass surface plates (each of area 50 sq. cm.) placed horizontally and separated from one another to a distance of about 0·6 mm. by three very small accurately gauged distance-pieces of ebonite. This small condenser was kept in a desiccator, and out of this the leads were carried in an air-tight manner through ebonite tubes ringed with sulphur for better insulation. The capacity of the air condenser was first measured and then the dry sheet of paper was slipped between the plates, and the altered capacity was tested. From these measurements the specific inductive capacity (k) of the paper was deduced as follows:—

Let b = distance between the plates;
$= b_1 + b_2$, where b_1 and b_2 refer to air and paper respectively;
s = area of paper between plates.

Let K_1 and K_2 be the observed capacities. If K = capacity for area s with air only, then, neglecting edge action,

$$K = \frac{s}{4\pi b \times 900{,}000} \text{ mfds. and is thus known;} \qquad \text{let } K = \frac{a}{b}.$$

Now $$K_1 = x + \frac{a}{b}, \quad \text{and} \quad K_2 = x + \frac{a}{b_1 + b_2/k}.$$

Let $$Q = \frac{K_2 - x}{K_1 - x};$$

then $$Q = \frac{b}{b_1 + b_2/k}, \quad \text{or} \quad k = \frac{b_1}{b/Q - b_1}.$$

Hence $$k = \frac{K_2 - K_1 + K}{K b_2/b_1 - K_2 + K_1}. \qquad (1)$$

* This method was used by Mr. Packer, of the British Insulated Wire Company, in a series of paper tests made in 1901.

Measurement of Capacity.—The measurements of capacity were made by Maxwell's method,* the connections being shown in fig. 1.

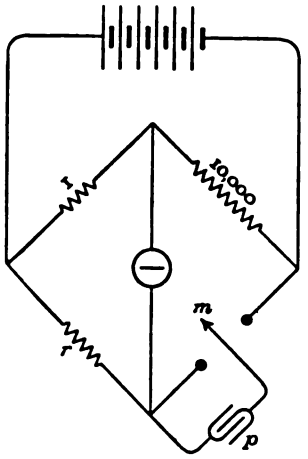


FIG. 1.

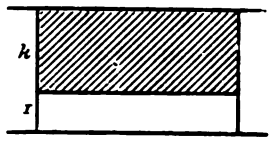


FIG. 2

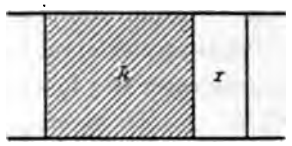


FIG. 3.

By a rotating contact-maker, the moving part of which is represented by m, the condenser p is charged and short-circuited with a frequency of n per second; during the charge only it forms one arm of the Wheatstone's bridge shown. A moving coil galvanometer of slow period is used, the resistance r is set so as to give nearly a balance, and then the speed of the contact maker is kept at such a value as to hold the light-spot at zero. The capacity was calculated by the usual formula, a deduction being made for the capacity of the commutator and leads (found by a blank experiment). The voltage used was about 40 volts.

Correction for Conduction.—In nearly every instance readings were taken with at least two frequencies (usually about 20 and 40 $\sim$ per second). Sometimes the apparent capacity was found to vary with the frequency, being greater at the lower frequency; this is due to conduction in the condenser, which behaves as a pure capacity shunted by a high resistance. When the conduction was not negligible, a correction for it was applied, the capacity and resistance being separated in the following way:—

Let K and R be the true capacity and resistance respectively; and let K_1 and K_2 be the apparent capacities for frequencies n_1 and n_2.

The commutator inserts the condenser in one arm of the bridge during a certain fraction of each revolution; let this fraction $= \sigma$. The value of σ may be obtained by measurements at the rim of the commutator.

* As used by Professor J. J. Thomson, Mr. Searle, Dr. Glazebrook, and others.

We have $\frac{\sigma}{n_1 R}+K=K_1$, and $\frac{\sigma}{n_2 R}+K=K_2$.

Hence
$$K=K_1-\frac{n_2}{n_1-n_2}(K_2-K_1), \tag{2}$$

and
$$R=\frac{n_1-n_2}{n_1 n_2}\left(\frac{\sigma}{K_2-K_1}\right). \tag{3}$$

In order to test these formulas, a condenser of capacity 1·011 mfd. (with high insulation) was shunted (*a*) by 100,000 ohms, (*b*) by 10,000 ohms, and the apparent capacity in each case was measured for two frequencies (about 14 and 38 $\sim$ per second). Case (*b*) was chosen as an extreme one, the apparent capacities rising to about 2·3 and 4·7 mfds. respectively. The values of K obtained by equation (3) from tests (*a*) and (*b*) were 1·020 and 1·009 mfd. respectively.

From (*a*), taking R = 0·1 megohm, σ was found by (4) to be 0·463, whilst measurements of the commutator gave $\sigma \fallingdotseq 0{\cdot}446$. From the results of (*b*), using $\sigma = 0{\cdot}463$, equation (4) gave R = 0·00100 megohm, agreeing with its known value. These results show that even in extreme cases the equations (2) and (3) may be used.

Test with Small Air Condenser.—The capacities which had to be measured were all very small, being from 0·0002 to 0·001 mfd., and the correction for the leads and commutator amounted to about 0·00001 mfd. Besides, no correction was applied for the edges of the plates,* which were without guard rims.

For these reasons the method was checked by applying it to test a small air condenser, the capacity of which was of the same order as the paper condensers to be tested. This air condenser was built up of two pieces of plate glass (each of about 100 sq. cm. area), silvered on the sides that faced one another, and separated by minute distance-pieces of ebonite or dry paper. The distance between the plates was from 0·03 to 0·05 cm., and was measured by gauging the distance-pieces. The conduction by surface leakage over the distance-pieces was relatively considerable, and had to be corrected for as described above. The values found by experiment were compared with those calculated from the measured dimensions, and the agreement was quite satisfactory, *e.g.*—

Calculated, mfd.	Observed, mfd.
0·000243	0·000244
0·000153	0·000153

* It appears that no complete mathematical treatment of the simple plate condenser has yet been carried out.

Measurement of Thickness.—The thickness of each sheet was tested immediately after the capacity measurements. As the surface of the paper presents much irregularity, it is a very difficult matter to find the average thickness. After several other arrangements had been tried, it was decided that an ordinary screw gauge was as good as any, and it was used throughout. The contact ends of this gauge had each an area of about 0·2 sq. cm., while the safety ratchet head applied a pressure of about 1 kgm. per square centimetre. As this pressure is about three times that applied to the indiarubber discs in method (A), it is probable that the increased compression will tend to make some allowance for the tinfoil penetrating the irregularities of the paper surface.

Results of Tests.—In Table I are given some of the results. A few of the samples were tested by method (A), both with a single sheet and with a pile of three sheets; the latter tests are included in the table.*

Table I.

Sample number.	Approximate thickness.	Specific inductive capacity.		
		By tinfoil clamps.		By plate condenser.
		From 1 sheet.	From 3 sheets.	
	mm.			
14	0·08	2·5	2·6	
15	0·12	1·8	—	1·8
54	0·13	1·9	1·9	
49	0·18	2·1	2·2	
9	0·19	2·3	—	2·1
17	0·25	1·9	—	2·0
18	0·25	2·0	—	1·8
56	0·28	1·8	—	1·7
58	0·28	2·0	—	1·9
2	0·5	2·2	2·3	

From the foregoing table it will be seen that the two methods show as good agreement as could be expected from the nature of the material, but there is considerable variation from sample to sample. By weighing six samples it was found that their specific capacities were nearly in the order corresponding to that of their densities, which varied from 0·55 to 0·78. It was suggested that it would be of interest to compare the above values of specific inductive capacity with that for solid cellulose. As no data for the latter appeared available, a research (which forms the third part of this

* A sample of special black paper (partly parchmentised), kindly supplied by Mr. Clayton Beadle, gave $k \fallingdotseq 2{\cdot}3$.

paper) was undertaken upon the electrical properties of solid cellulose Its specific inductive capacity was found to be about 6·8. Now, when the cellulose fibres (which we shall assume to form the whole solid part of the paper) are assembled with a certain amount of air space between them, the specific inductive capacity (k_p) of the resulting paper depends very largely upon the relative arrangement of the air and the cellulose. The following simple investigation will illustrate this point:—

Let d = density of cellulose (about 1·50), D = that of paper, 0 = that of air, q = ratio of cellulose volume to air volume.

Then
$$q = \frac{D_1}{d - D_1} = \frac{D_1}{1{\cdot}50 - D_1}, \tag{4}$$

and thus q can be found by experiment.

Now, for a given value of q, it will be found that k_p is least when the cellulose and air are in strata parallel to the condenser coatings, and greatest when these strata run at right angles to the coatings. These cases are represented sufficiently by figs. 2 and 3. Let k_1 and k_2 be the resulting specific inductive capacity in these cases respectively.

It is easy to show that
$$k_1 = \frac{(1+q)\,k}{q+k}, \tag{5}$$

and
$$k_2 = \frac{1+kq}{1+q}. \tag{6}$$

By weighing and gauging a number of the samples the value of q was found for each; from these values the minimum and maximum k_1 and k_2 were calculated. From Table II it will be seen that the actually observed values of k_p all lie below the mean of k_1 and k_2. This indicates (electrically) that the fibres of cellulose are arranged more in a direction parallel to the surfaces of the paper than at right angles to it, which is otherwise known to be the case.

Table II.

q.	k_1.	k_2.	$\frac{1}{2}(k_1+k_2)$.	Observed k_p.
0·577	1·45	3·12	2·28	1·93
0·629	1·49	3·23	2·36	1·89
0·843	1·64	3·65	2·70	2·21
0·930	1·70	3·79	2·75	2·25
1·078	1·79	4·02	2·90	2·30

It is clear that the law of mixtures found by L. Silberstein* does not apply here.

* 'Wied. Ann.,' vol. 56, p. 661, 1895.

Table II is of interest in connection with practical telephone work, in which the lowest possible value of the mean specific inductive capacity is aimed at. From the values of k_1 and k_2 we see that the mean resultant k depends very much on the relative positions of the paper fibres and the air spaces. The numbers in Table I give about 2·0 as a mean value for the specific inductive capacity of dry telephone paper, and this is in fair agreement with results already published by other observers. Signor E. Jona, by testing dry paper between metal plates, found k approximately equal to 2·0. Herr M. S. von Pirani* gives $k = 2{\cdot}0$ to 2·6, but he does not indicate clearly the conditions of his tests.

Part II (supplied by Mr. Gavey).—Additional Data and Tests on Cables

The undermentioned samples of oven-dried paper have been tested, with the results shown in Table III.

Table III.

Sample number.	Weight of ash, per cent.	Proportion by volume.	
		Fibre, per cent.	Air space, per cent.
9	1·37	49·0	51·0
15	1·45	35·0	65·0
17	1·80	36·0	64·0
18	1·11	36·5	63·5
56	0·96	32·5	67·5
58	1·70	36·0	64·0

The thickness of the papers was measured with a screw gauge which exerted a pressure of about 1·5 kgm. per square centimetre on the paper when the safety ratchet was used. It was found that the thickness of the paper measured with this pressure, and also with that of a light touch with the fingers on the screw gauge, differed by 10 per cent., *i.e.*, the air space figures given above would have been 6 per cent. higher if the ratchet were not used. It was also found that the thickness of the paper when several sheets were measured together was 2 to 3 per cent. less than when measured in single sheets.

The method finally adopted was to measure single sheets, using the ratchet referred to above, which it was thought would approximate as closely as was possible to the conditions observed by the National Physical Laboratory.

The figures used for the density of fibre and ash were 1·5 and 2·0

* 'Berlin Dissertation,' 1903.

respectively. From the weights per cubic centimetre and the respective densities, the volume of fibre and air space in each paper was calculated.

The samples of paper, although classed commercially as "Manilla" papers, on microscopic examination proved to be composed of mixtures of chemical wood pulp and hemp in different proportions. There was no trace of lignified fibres or mechanical wood. The minimum breaking stress specified by the Post Office for papers of this class is 4000 lbs. per square inch, but 7000 lbs. per square inch is about the average value obtained (*i.e.*, about 490 kgm. per square centimetre).*

With the kind assistance of Messrs. W. T. Henley's Telegraph Works Company, Limited, an attempt has been made to determine the effect of temperature on the electrical properties of the combination of air and dry paper as found in telephone cables. The results are indicated graphically in the curves in figs. 4 and 5, showing the variation of insulation-resistance and capacity respectively with temperature.

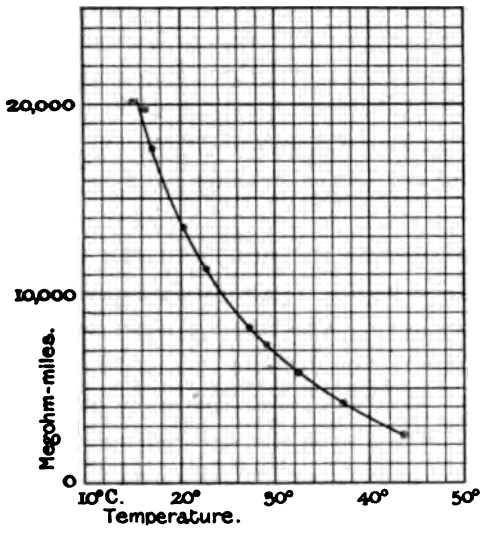


Fig. 4.—Variation of Insulation-Resistance with Temperature in Air Space Paper Core Cable (P.O.).

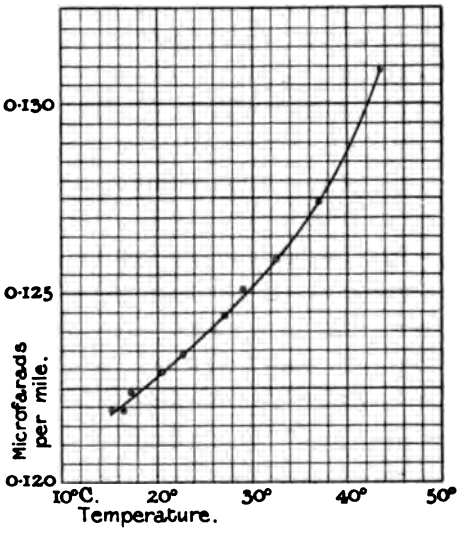


Fig. 5.—Variation of Capacity with Temperature in Air Space Screened Cable (Post Office Type).

* The construction of a paper-screened telephone cable is as follows:—The conducting wires are wrapped loosely in longitudinal (not spiral) strips of thin paper: two or more wires thus covered are placed together and thoroughly dried in an oven. While they are still dry and warm, a covering of lead is applied by a lead press, and in this way the moisture from the outside air is excluded. The paper merely acts as a mechanical separation between the conductors (and the lead sheath). As the lowest possible electrical capacity is desirable, anything that tends to decrease the permittivity of this separating medium is of practical advantage.

The proportion of air space and paper in the cable to which these tests refer was approximately 26 per cent. air, 74 per cent. paper.

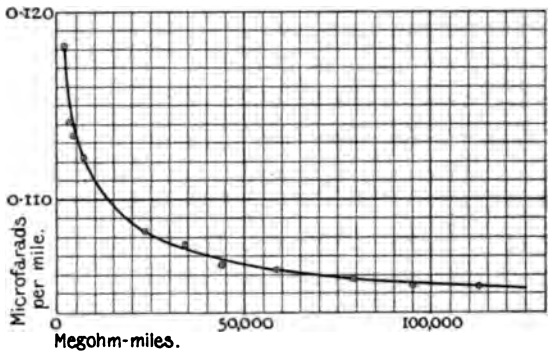


FIG. 6.—Variation of Capacity with Insulation-Resistance in Air Space Paper Screened Cable (Post Office Type).

The curve in fig. 6 was obtained with the kind assistance of the British Insulated and Helsby Cables, Limited, and shows the variation of capacity with the amount of uniformly distributed moisture in a cable as measured by the insulation-resistance. Each wire in this cable was insulated with paper and then covered with a copper tape wrapped on spirally. The cable was tested before being sheathed with lead, the copper tape making a sufficiently good earth.

The method adopted was as follows:—The cable was first dried and then allowed to stand exposed to the air for over a week. The moisture in the air penetrated through the interstices in the copper tape, making the paper damp, and tests were taken periodically to determine the capacity and insulation-resistance. The ends were kept well waxed and tests taken with and without a guard wire showed there was no leakage at the ends.

The proportion of air and paper in this cable was about 31 per cent. air, 69 per cent. paper.

The capacity in each case was measured by the comparison on a galvanometer of the charge deflection from the cable with that from a standard condenser. No correction has been applied for leakage, but the error was found to be about $1\frac{1}{2}$ per cent. on the capacity corresponding to 5000 megohm-miles, and $2\frac{1}{2}$ per cent. on the capacity corresponding to 2000 megohm-miles. This would reduce the alteration in the Temperature-Capacity Curve between the limits of temperature shown from $7\frac{1}{2}$ to 5 per cent.

It is suggested that the reason of the alteration in the capacity with increasing temperature may in some part be due to the absorption of the moisture in the paper by the hot air, thus altering the distribution of the

dielectrics in the cable. This view is somewhat borne out by the fact that another cable which was dried to an insulation-resistance of 140,000 megohm-miles, and therefore contained less moisture, has only 2 per cent. difference in the capacity between the same limits of temperature.

Part III.—Solid Cellulose.

A series of tests were made on a number of samples of nearly pure cellulose kindly supplied to the laboratory by Mr. C. F. Cross.

The material was prepared by the following process:—Crude viscous 10-per-cent. solution of cellulose xanthogenic acid (sodium salt), with alkaline by-products, was spread on a glass plate, dried at 60° C., salted out with pure brine to remove soluble by-products, and the cellulose finally "fixed" and purified by treatment with acid and thorough washing.

The samples were in the form of fairly uniform translucent sheets from 0·06 to 0·3 mm. in thickness. For most of the experiments the sheets were dried for several days in an oven at 80° to 110° C. As the air-dry material is of the nature of a colloidal solution, the thorough drying is a long process, and the reabsorption of moisture from the atmosphere is very much slower than in the case of fibrous cellulose like paper. In the first experiments clamps of indiarubber and tinfoil were used, but it was found that these did not make satisfactory contact with the very smooth surface of the cellulose; they were therefore discarded and were replaced by mercury clamps* consisting of troughs with indiarubber edges pressed against opposite sides of the sheet and filled with mercury. The clamps and the mercury were usually dried in the oven and applied while still hot, a set of tests being taken as the whole apparatus cooled down to the temperature of the room. Capacity tests made on mica sheets of two different thicknesses gave concordant results and so proved that the mercury contacts were satisfactory. The drying made the cellulose very brittle, but immersion in water restored it to the flexible condition. Some of the capacity measurements were made by Maxwell's method (as already described), but in order to avoid polarisation and minimise the effect of conduction the method† shown in fig. 7 was usually employed.

S is a small standard condenser, K the condenser to be tested, R_1 and R_2 variable resistances, while M is a telephone-plate sounder‡ (giving 800 $\sim$ per second), such as is sometimes used in place of an electric bell. The intermittent current from M gives, by means of the transformer T, an

* See R. Appleyard, 'Proc. Phys. Soc.,' p. 724, vol. 19, December, 1905.

† Used by Nernst and others.

‡ An "Electric Trumpet" supplied by The General Electric Company.

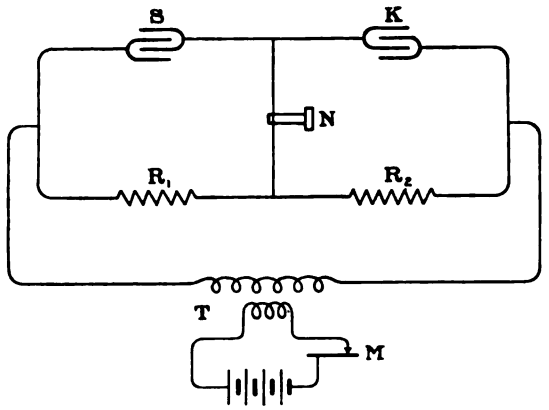


FIG. 7.

alternating current in the bridge SKR_2R_1. The ratio R_1/R_2 is altered until there is silence in the telephone N; then $K/S = R_1/R_2$. When the cellulose was thoroughly dry, the point of balance was quite definite, but when it was only air-dry, a point of minimum sound was all that could be obtained (but see below). The results obtained from sheets of different thicknesses (0·06 to 0·3 mm.) were in very fair agreement both for capacity and resistivity throughout a considerable range of temperature. The resistivities were measured by the method of direct deflection at 200 volts with 1 minute's electrification. Table III gives mean results for a range of temperature from 70° down to 20° C., and figs. 8 and 9 give the corresponding curves. (The resistivities with 2 minutes' electrification were 20 to 30 per cent. higher.)

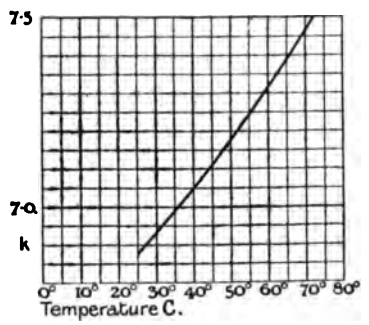


FIG. 8.—Oven-dried Cellulose. Specific Inductive Capacity.

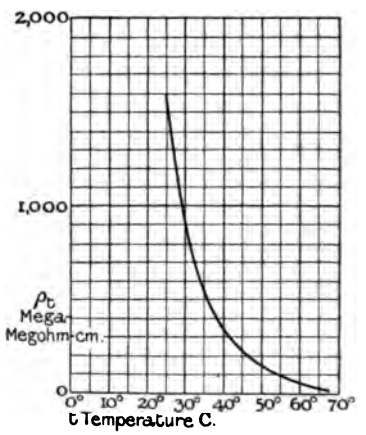


FIG. 9.—Oven-dried Cellulose. Apparent Resistivity by Direct Deflection Method.

Table IV.—Dry Cellulose.

Temperature.	Sp. ind. capacity.	Resistivity.
° C.		megohm-cm.
20	6·7	
25	—	1600×10^6
30	6·8	900×10^6
40	7·0	330×10^6
50	7·2	125×10^6
60	7·3	40×10^6
65	—	20×10^6
70	7·5	

Part IV.—Tests on Damp Cellulose.

The influence of moisture upon the electrical properties of paper (illustrated by the curve of fig. 6) is striking. Some years ago I observed that, when even a trace of moisture was present, a sudden lowering of the temperature always caused a considerable increase in insulation-resistance.*

At that time I advanced the theory that the effect was largely a mechanical one, the lowering of temperature causing the moisture to be drawn into the hollow tubular interiors of the fibres. Since the solid cellulose is not of fibrous structure, it was of interest to try its behaviour when in the "air-dry" condition, *i.e.*, after exposure to the atmosphere for a considerable time. Of course, the amount of moisture present depends on the humidity of the air, the temperature, etc., and therefore the conditions vary from day to day; thus the results refer only to the actual conditions holding at the time of the particular experiment. In each case the cellulose was placed between the clamps, hot mercury was poured in, and observations were made during the cooling. Tests of apparent resistivity were made by observing the current due to a constant potential difference kept continuously applied. Fig. 10 gives an example of a curve thus obtained. As might be expected, strong polarisation effects made their appearance. When attempts were made to measure the capacity by Maxwell's method the polarisation caused a large displacement of zero, and made it impossible to obtain any true result. With the telephone method of fig. 7 the relatively good conductance of the specimen made it impossible to obtain a balance. However, by shunting the standard condenser S (as shown in fig. 11) by a variable resistance X, it was always possible to get a good balance.

* See E. H. Rayner, 'Proc. Inst. Elec. Eng.,' p. 625, vol. 34 1905.

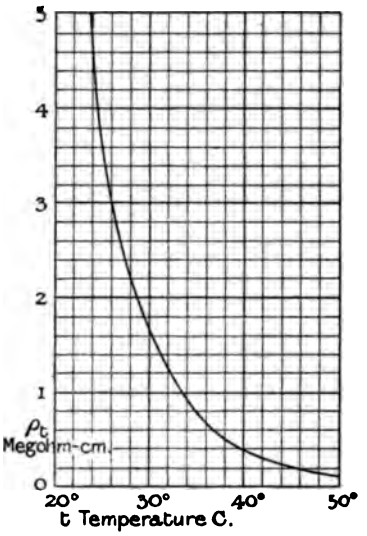


FIG. 10.—Air-dry Cellulose. Apparent Resistivity by Direct Deflection Method.

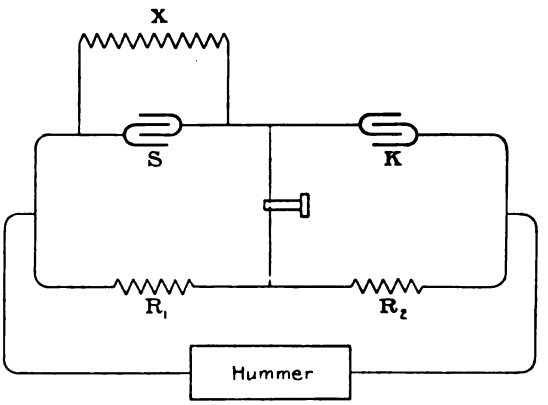


FIG. 11.

As high frequency is desirable, the source of current was a microphone hummer* of special construction giving 2000 ~ per second. The arrangement of this is shown in fig. 12. A is a rod of mild steel (or tool steel) supported horizontally at nodal points, and carrying at one end a very light microphone B shunted by a condenser C. T is a transformer whose secondary is connected to the coil of a polarised telephone magnet M. If A is set vibrating by a blow, the pulsating current in the microphone circuit gives an alternating current round M, and so maintains the vibration.

* For earlier microphone hummers see the following :—R. Appleyard, 'Elec. Review, pp. 57 and 656, vol. 26, 1890 ; J. E. Taylor, 'Inst. of Elec. Engs.,' p. 396, vol. 31, 1901 ; and F. Dolezalek, 'Zeitschr. für Instrumentenkunde,' p. 240, August, 1903.

The testing current is taken from another secondary winding of T. A mild-steel rod 2·5 cm. in diameter and 23·7 cm. long gives 2000 ~ per second. By using a shorter rod a frequency of 3000 to 4000 can be attained.

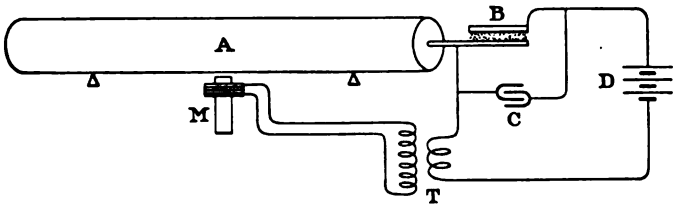


FIG. 12.—Microphone Hummer for 2000 ~ per second.

When the telephone is silent $K/S = R_1/R_2 = X$ divided by insulation resistance of K.

In fig. 13 is shown the variation of capacity with temperature for a sample of air-dry cellulose, suddenly heated and allowed to cool slowly.

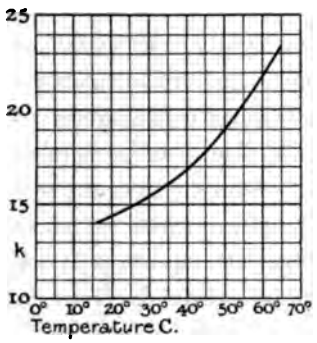


FIG. 13.—Air-dry Cellulose. Sp. Inductive Capacity.

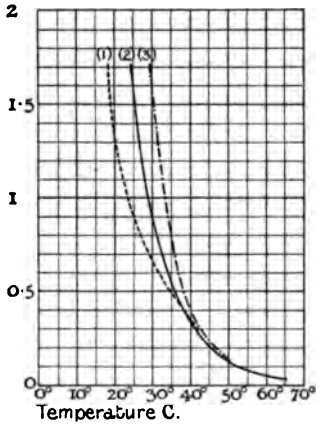


FIG. 14.—(1) Cable, (2) Oven-dried Cellulose, (3) Air-dry Cellulose.

From the values of the shunt X required to give a balance, the values of the insulation resistivity of K at the various temperatures can be obtained. Measurements made with the high frequency ($n = 2000$ ~ per second) at room temperatures gave values of the resistivity about 10 times smaller than the apparent resistivity shown by the steady deflection method (as in fig. 10); the variation with temperature was also much less with the high frequency alternating current. It may be mentioned that in the direct deflection test the immediate deflection fell off 10 to 15 per cent. after 1 minute's electrification. In telephone work the frequencies are high, and therefore it is the lower values of the resistivity that would occur when leakage due to moisture happens.

The matter, however, seems to want further investigation.

It will be seen from fig. 13 that when air-dry cellulose is quickly heated the specific inductive capacity increases very considerably. If the raised temperature is maintained and the moisture allowed to escape, the capacity gradually falls to a value dependent on the temperature. Since the material is not porous in the same sense that paper is, the mechanical theory based on the tubular nature of the fibres is thus excluded. The observed facts seem to indicate that a part of the moisture is chemically combined with the cellulose, the whole forming an electrolytic solution (possibly of water in cellulose hydrate). When the temperature is raised, partial *dissociation* appears to occur and, with continued steady temperature, dissociation equilibrium is attained. High specific inductive capacity and low resistivity would thus correspond to the presence of a relatively large amount of dissociated moisture present throughout the material.

Dielectric Strength of Solid Cellulose.—A number of sheets of cellulose, from 0·06 to 0·3 mm. thick, were tested for break-down voltage, both air-dry and oven-dried specimens being tried. The apparent dielectric strength (*i.e.*, $V_{max.}$ divided by thickness in centimetres) varied with the thickness of the sheet; for air-dry cellulose it was of the order of 250,000 volts per centimetre, and for oven-dried material 500,000 volts per centimetre.

Cellulose Acetate.—As cellulose acetate is coming into common use as an insulating material for covering thin wires, its electrical properties are of practical interest. It was therefore thought desirable to make a few tests upon it with a view to comparing its properties with those of cellulose. The acetate is soluble in chloroform, and by pouring the solution on to a glass plate a smooth and tough film may be obtained. Two specimens were tested namely:—

(*a*) Normal tri-acetate (kindly supplied by Mr. C. F. Cross).

(*b*) A sample from a German source, said to contain both tri- and tetra-acetate; it was found to contain also a small amount of sulphur in combination, probably SO_4H residue. By more recent methods of acetylation these products are more economically obtained: the acetylizing mixtures contain sulphuric acid, and a proportion of SO_4H residues is fixed together with the acetyl.

Sample (*a*) when air-dry gave a specific inductive capacity of about 4·7; when oven-dried the value was about 3·9. The variation with temperature was scarcely perceptible, being of the order of one per cent. for 40° C. Sample (*b*) gave less consistent and somewhat higher values.

The resistivities were also determined approximately, the result at 200 volts with one minute's electrification being given in Table V.

Table V.

Material.	Condition.	Temperature.	Resistivity.
		° C.	Mega-megohm-cm.
Cellulose acetate (*a*).....	Air-dry	16·5	200
„ „	Oven-dried	26·0	over 9000
Cellulose acetate (*b*).....	Air-dry	26·0	13
„ „	Oven-dried	26·0	121

General Remarks.—On comparing the temperature-capacity curves for the cable and the dry cellulose sheet, it will be found that the rate of variation of capacity with temperature is about 50 per cent. greater in the cable than in the sheet; this indicates probably that the paper of the cable was not dried to such an extreme extent as the cellulose sheet. The air-dry cellulose, on the other hand, has a very much larger k to start with and this increases very rapidly with temperature (if the moisture be kept from escaping).

With regard to the resistivities, the curves of figs. 4, 9, and 10 have been brought together in fig. 14 (by altering the scales) so as nearly to coincide at 40° C. It will be noticed that between 30° and 40° C. the cable shows the least, and the air-dry cellulose the greatest variation with temperature. This is probably due to the fact that in the cable the moisture can partially escape into the air spaces. It is curious to find, for the dried cellulose, that while the capacity does not alter much with temperature, the insulation alters enormously. This leads to the inference that in spite of the extreme drying (to brittleness) the alterations with temperature are still due to dissociation of combined moisture. The amount of this moisture may be very infinitesimal when we remember that the drying raises the resistivity 300 million times. With regard to the cellulose acetate, even in its air-dry condition it is a good insulator. Its specific inductive capacity also is lower than that of cellulose. It is evident, therefore, that it is far less susceptible to the effects of moisture than either paper or solid cellulose.

In conclusion, I must express my hearty thanks to all who have aided me in the above investigation; to Dr. Glazebrook for constant and valued advice and help; to Mr. Gavey and his colleagues, Mr. H Hartnell and Mr. A. G. Lee, for all the data in Part II, some of which were obtained expressly for this paper; to Mr. C. F. Cross for all the material used in the cellulose tests and for kind advice; to Signor E. Jona for valuable information; and to Dr. W. A. Caspari and Mr. W. Gemmell for help in connection with the chemical part of the subject.

Note on the Production of Secondary Rays by α Rays from Polonium.

By W. H. Logeman, M.A., Fellow of the University of the Cape of Good Hope; 1851 Research Scholar of the South African College, Cape Town; Trinity College, Cambridge.

(Communicated by Professor J. J. Thomson, F.R.S. Received June 25,—Read June 28, 1906.)

In the 'Philosophical Magazine' for May, 1896, Professor Bragg points out that since the α rays are absorbed by a solid according to the same law as by a gas, it seems reasonable to expect that the atoms of the solid are ionised in the same manner as are those of a gas. Hence we should expect that slowly-moving negative rays would be given off at the surfaces where the α rays enter or leave a solid. Professor J. J. Thomson has shown* that when a solid is subjected to bombardment by a stream of canalstrahlen, it emits cathode rays.

In the course of some experiments which were undertaken with the idea of determining the velocity of projection and the ratio of the charge to the mass of the slowly-moving negative or δ rays emitted by polonium, the writer has obtained some results which appear to indicate clearly the existence of slowly moving negatively charged secondary rays which are produced when an aluminium or copper plate is bombarded by a stream of α particles.

The apparatus used in these experiments is shown in the accompanying figure, p. 213.

A is a circular disc of copper, 4 cm. in diameter, coated on the side facing B with a thin deposit of polonium. This was obtained from Sthamer, of Hamburg.

B is an aluminium disc of the same diameter as A, and supported parallel to A by the stiff brass wire F. C is an ebonite stopper fitting into the narrow end of the glass tube G. Through C passes a brass tube E, inside which is fitted a second ebonite stopper J, supporting the wire F to which the plate B is attached. The dotted lines in the figure show where the tube is silvered inside to render its surface conducting. The disc A is supported centrally in the tube by means of three small metal feet projecting from its circumference and is rigidly attached by the wire loop L to the brass plate M which fits loosely in the tube. Contact can be made with the disc A by means of the flexible wire spiral N and the platinum wire terminal O. The distance between the plates A and B can thus be adjusted by tilting the tube and allowing the whole system ALM to slide inside.

* 'Camb. Phil. Soc. Proc.,' November, 1905.

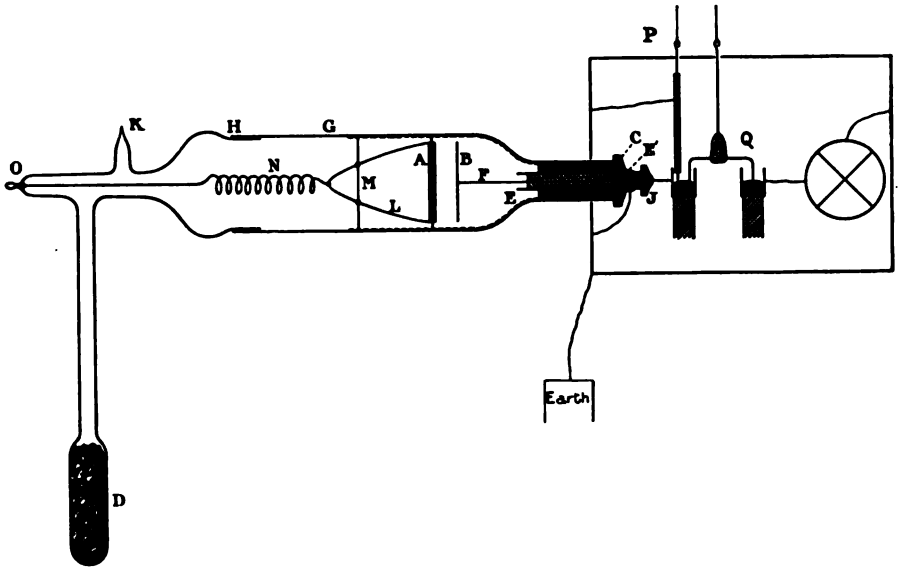


FIG. 1.

D is a glass bulb filled with pieces of hard charcoal for immersing in liquid air, in order to absorb as much as possible of the last traces of gas in the tube. The joints at C and H were made air-tight with sealing wax. The whole apparatus was attached to a mercury pump and evacuated down to a pressure of about 0·001 mm. of mercury, and then sealed off at K. Most of the readings were taken while the bulb D was surrounded by liquid air.

The plate B was connected to the insulated terminal of a quadrant electrometer through a mercury key with sulphur insulation in the manner shown in the figure, all the usual precautions being taken to shield the connections from external electrostatic fields.

The tube E was connected to earth, so as to form a guard ring, and prevent any direct leak from the silver lining of the tube (which was in metallic connection with the disc A) to the insulated wire F.

The method of taking observations was as follows:—

The polonium disc was first brought to the required potential by connecting it with a battery of small secondary cells. The earth connection at R was then broken by raising the wire P. Exactly one minute later the connection between B and the electrometer was broken by raising the bridge-piece Q, and B was earthed again by lowering the wire P. Half a minute was allowed for the spot of light to come to rest, and the reading was then taken.

The tube was placed with the gap AB between the poles of an electromagnet, so that different strengths of magnetic field could be applied at right angles to the line joining the centres of the discs A and B. The sensitiveness of the electrometer was about 800 divisions per volt.

The following two tables of results may be taken as typical:—

Table I.

(Distance between discs = 5 mm.)

Strength of magnetic field.	Potential of polonium.	Reading.
C.G.S. units.	volts.	Scale divisions.
0	0	− 58·0
0	+ 2	+ 86·0
0	+ 4	+138·0
0	+ 6	+169·0
0	+ 8	+176·5
0	+10	+181·5
0	+12	+182·0
0	+14	+185·0
8	0	− 31·5
20	0	− 5·0
32	0	+ 9·0
45	0	+ 16·0
59	0	+ 18·5
72	0	+ 21·0
85	0	+ 22·5
98	0	+ 24·0
111	0	+ 26·0
125	0	+ 26·5
153	0	+ 27·5
178	0	+ 29·5
202	0	+ 30·5
350	0	+ 33·0

Table II.

(Distance between discs = 10 mm.)

Strength of magnetic field.	Potential of polonium.	Reading.
C.G.S. units.	volts.	Scale divisions.
0	−20	−298·0
0	−14	−286·0
0	−12	−277·0
0	−10	−268·0
0	− 8	−252·0
0	− 6	−232·0
0	− 4	−196·0
0	− 2	−143·5
0	0	− 56·0
0	+ 2	+ 57·0
0	+ 4	+ 88·0
0	+ 6	+100·0
0	+ 8	+103·5
0	+10	+107·5
0	+12	+108·5
0	+14	+109·0
0	+20	+110·0
700	+20	+ 31·5

It is important to note that ordinary ionisation can have nothing to do with these results, as the pressure in the tube was far too low to allow of any appreciable amount of ionisation. This is shown to be the case by the fact that when the liquid air was removed and the carbon allowed to acquire the temperature of the surrounding air, the only observable change was a very slight diminution in the charge acquired by B.

These results are shown graphically in the three curves on p. 216.

From these figures and curves it is seen :—

(1) That under ordinary conditions, *i.e.*, when not acted upon by an electric or magnetic field, the polonium gives off a larger amount of negative than of positive rays.

(2) Under the influence of a gradually increasing electric field more and more of the slowly moving negative rays are stopped, and the charge carried by the α rays becomes more and more predominant.

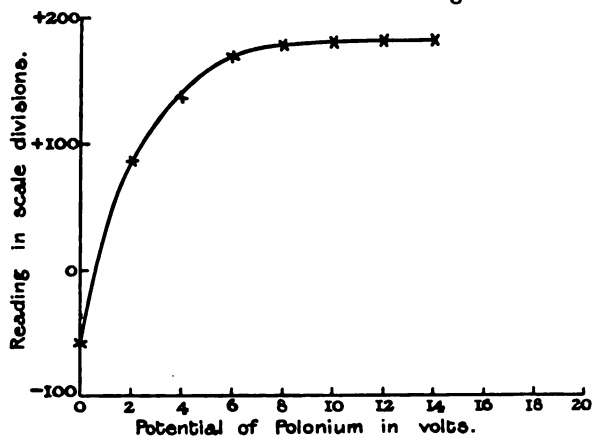
(3) A potential difference of about 10 volts between the plates is sufficient to stop the last of the δ rays. The fact that the Curve No. I goes on rising slightly for values of the abscissæ higher than 10 volts is easily accounted for on the supposition that a few of the oblique α rays which previously just missed the plate B get pulled in when the field is increased.

(4) The slowly moving negative rays can also be prevented from reaching the plate B by curling them up in a magnetic field. The fact that the Curve No. II continues to rise for values of the magnetic field above 100 C.G.S. units is very difficult to account for in view of the results obtained by Ewers,* according to which a field of 100 units should curl up the δ rays into circles of about 2 mm. diameter or spirals (in the case of those shot off obliquely) of still smaller diameter.

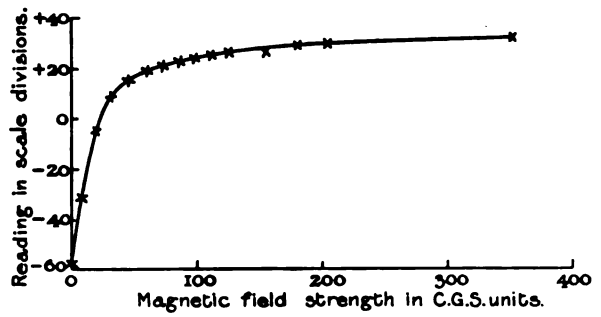
(5) The point of special interest for our present purpose is this: The limiting value of the positive current across the gap from A to B when the δ rays are stopped by a magnetic field is only about one-fifth of that obtained when an electric field is used to stop the δ rays. This fact appears to the writer to admit of only one interpretation, viz., when the potential difference between the plates is 10 volts or more (A being the positive plate) the positive current from A to B consists of the following two parts: First, a stream of α particles travelling from A to B. Second, a stream of negatively charged particles travelling from B to A. The magnetic field curls up this latter stream of negative rays, as well as the δ rays emitted by the polonium. This theory fits in well with the last two observations given in Table II. Here we have the polonium plate at a potential of +20 volts and the current between the plates (consisting of the two parts mentioned above) is

* 'Phys. Zeitschr.,' March 1, 1906, pp. 148—152.

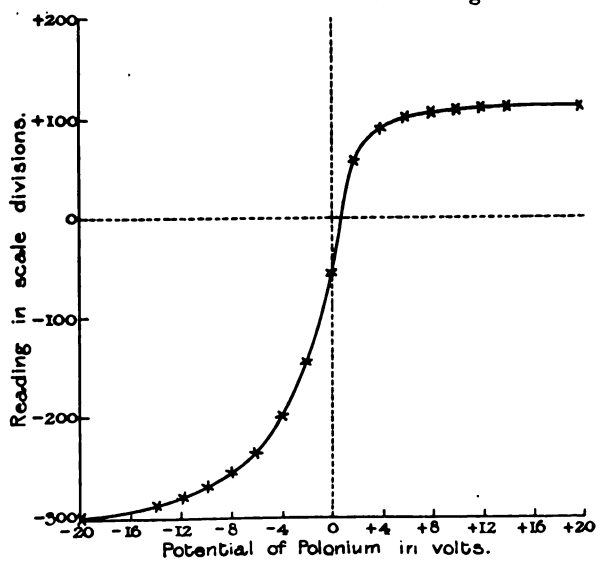
CURVE I.—5 mm. between discs. No magnetic field.



CURVE II.—5 mm. between discs. Polonium disc earthed.



CURVE III.—10 mm. between discs. No magnetic field.



represented by the number 110. A magnetic field is then brought into play of such strength as to prevent the negative particles which leave B from reaching A, and to make them return to the plate B. The current is thus cut down to a value represented by 31·5.

Very similar results were obtained when the aluminium disc B was replaced by one made of copper.

There is one other respect in which the above results are difficult to reconcile with those obtained by Ewers. According to his figures for the velocity and ratio of the charge to the mass of the δ rays, a potential difference of 30 volts should be required to stop those shot off normally. As will be seen, this is far from the case with the sample of polonium used by me.

I hope before long to be able to publish results giving the values of v and e/m for the δ rays from my sample of polonium, and also for the secondary rays, the existence of which is proved above.

In conclusion, I have to thank Professor Thomson for his kind interest, and his readiness to assist me with his advice throughout these experiments.

Researches on Explosives. Part IV.

By Sir A. Noble, Bart., K.C.B., D.Sc. (Oxon), D.C.L., F.R.S., etc.

(Received and read June 28, 1906.)

[Plate 6.]

(Abstract.)

In Part III of my "Researches on Explosives," I gave the results of a very extensive series of experiments, the completion of which necessarily occupied a very long time, and the particular explosives with which I experimented were those with which artillerists in this country were familiar, and with which a considerable number of experiments had been made.

These explosives were, first, the cordite of the Service, known as Mark I second, the modified cordite, known as M.D.; and third, the nitrocellulose, known as Rottweil R.R. The experiments made by myself extended, for all the above explosives, from densities of 0·05 to 0·45 or 0·50, and pressures of from 2·75 tons per square inch (419 atmospheres) to pressures of 60 tons per square inch (9145 atmospheres).

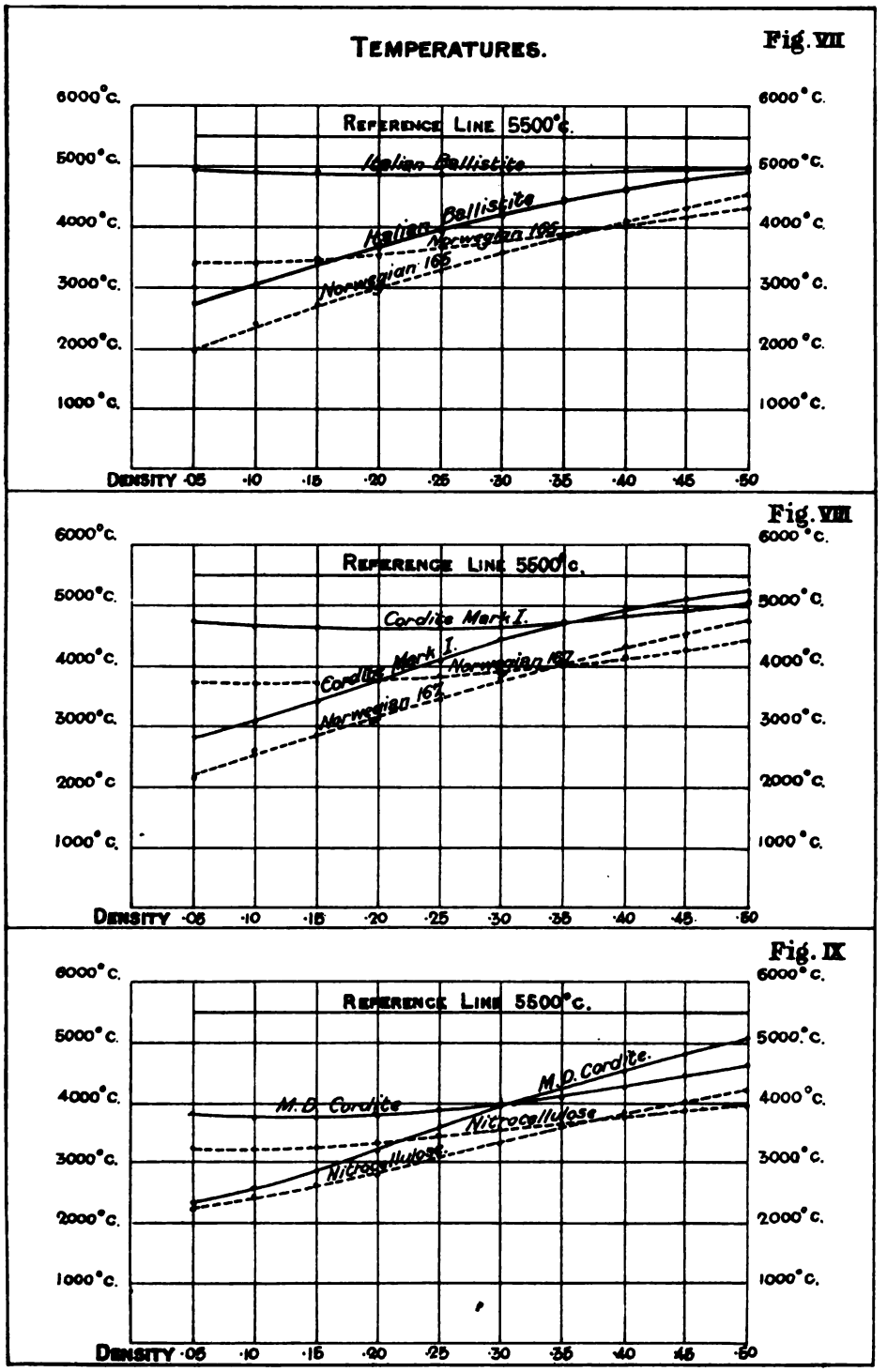
The composition of the various explosives referred to are given, and experiments quoted to show that the transformation experienced on explosion at different densities is practically identical.

When explosives are fired in a gun, the chamber in which the charge is placed is, of course, full of air, and in my experiments the charges were similarly treated, but, to test the resulting differences, charges were fired at the lowest densities in air, in nitrogen, and *in vacuo*, and the analyses of the products of explosion are given, and compared with the analyses of gases taken from the chamber of a gun after discharge.

Although for the elucidation of the laws which govern the transformation of the explosives when fired I have taken the densities named, I must point out that the requirements of the artillerist are confined to much narrower limits, the density, of course, varying considerably with the particular explosive used.

In modern guns, for example, the chamber density varies from about 0·310 to nearly 0·500, a good deal of the variation being due to the nature of the explosive used. It is hardly necessary to point out to artillerists that the chamber density is not the density which is responsible for the pressure developed in the gun.

The difference, which is frequently very considerable, is due to the time


TEMPERATURES.
Fig. VII
6000°C.
5000°C.
4000°C.
3000°C.
2000°C.
1000°C.
REFERENCE LINE 5500°C.
Italian Ballistite
Italian Ballistite
Norwegian 16%
Norwegian 16%
DENSITY ·05 ·10 ·15 ·20 ·25 ·30 ·35 ·40 ·45 ·50
Fig. VIII
REFERENCE LINE 5500°C.
Cordite Mark I.
Cordite Mark I.
Norwegian 16%
Norwegian 16%
Fig. IX
REFERENCE LINE 5500°C.
M.D. Cordite.
M.D. Cordite
Nitrocellulose
Nitrocellulose

taken by the explosive to burn, and this depends upon the nature, form, and dimensions of the explosive, the expansion suffered by the nascent gases, and the heat lost, due to work done upon the projectile and by communication of heat to the gun, and, under these circumstances, the pressure developed would, with full charges, if compared with close-vessel pressures, represent densities approximately between 0·17 and 0·23.

The tables which are given in my late communication* to the Royal Society gave for each particular density the actual result observed. In the present paper the observations have been corrected by drawing curves to represent as nearly as possible the whole of the results, the actual observations, which are also given, showing in each case the departure from the curve. If reference be made to the tables,† it will be observed how wide are the differences between the explosives, not only in the absolute volumes of the several gases, but in the variations with reference to the densities at which they were fired.

Thus, for example, comparing Norwegian 165 and Italian Ballistites, while in the former the carbon monoxide commences at the density 0·05 with a percentage volume of 38·5, falling at a density of 0·45 to 22 per cent., the carbon dioxide commences with 13·3 per cent., rising rapidly to 31 per cent. In the latter explosive the CO commences at 20·5 per cent., and falls slowly to 15 per cent., while the CO_2 commences a little over 26 per cent., rising also comparatively slowly to nearly 34 per cent.

I may remark in passing that the Italian Ballistite is the only explosive with which I have experimented where, at low densities, the volume of CO_2 is greater than that of CO.

But there are, in these two explosives, other remarkable differences. Thus, in the Italian Ballistite, at a density of 0·05, the volume of methane, CH_4, is a mere trace, about 0·02 per cent., but it remains very much lower than is the case with any other explosive, being only 1·9 per cent. at the density of 0·45. With the Norwegian, on the other hand, the CH_4, although the volume at commencement is only 0·04 per cent., is, at 0·45 density, 11 per cent.

Again, as might be expected from the large quantity of CH_4 found in the case of the Norwegian Ballistite, the volume of hydrogen falls from over 20 per cent. to about 9 per cent.; in the Italian the H rises from about 8 per cent. to about 10 per cent., falling slightly at higher densities.

In both explosives the N is practically constant at about 12 and 16 per cent. respectively, but there is a very great difference as regards the

* 'Phil. Trans.,' vol. 205, pp. 221—223.

† Not given in this abstract.

H_2O. In the Norwegian the H_2O is constant at 14 per cent., there being no greater difference than might be expected from errors of observation, while in the Italian the H_2O, which commences at density 0·05 with a volume of 29 per cent., falls at a density of 0·45 to about 24 per cent. No other explosive approaches the Italian Ballistite in respect to the large volume of aqueous vapour formed, especially at low densities.

In the tables are given the volumes in cubic centimetres per gramme of the permanent and total gases, and curves have been drawn representing for the six explosives the observations of these volumes. In the case of five of the explosives there is, with increasing density, a very considerable decrease in volume, but with the Italian Ballistite, throughout the range of the experiments, there is hardly any change. Curves representing these volumes are concave to the axis of abscissæ.

In the tables are shown the units of heat, both for water fluid and water gaseous. Curves have also been drawn for the units of heat (water gaseous); the curves in this instance are all convex to the axis of abscissæ, and it may be noted that, where the volumes of gas per gramme are large, the units of heat are low, and that, where the volumes of gas are rapidly decreasing, the curves representing the amount of heat developed show a rapid increase.

The next point we have to consider is, the data being as shown in tables, what temperature are we to assign to that generated by the explosion? With the view of studying the question, I resorted to two methods: (1) knowing with very considerable accuracy the units of heat (water gaseous) generated by the explosion, and having determined approximately the specific heat of the gases, the temperature of explosion should be given by the equation

$$t = \frac{\text{gramme units of heat}}{\text{specific heat}} \qquad (1)$$

(2) Knowing also with considerable accuracy the pressure at any given density, and knowing the pressure p_0 when the volume of gas generated is reduced to the temperature of 0° C. and a pressure of 760 mm. of mercury, the temperature is given by the equation

$$t = \frac{p - p_0}{0{\cdot}00367 \cdot p_0} \qquad (2)$$

With reference to Equation (1), the specific heat of CO_2 is a very important factor in this determination, and the recent researches of Messrs. Holborn and Austin upon the specific heat of gases at constant pressure at high temperatures having apparently shown that the specific heats given by Mallard and Le Chatelier for temperatures above 100° C. are considerably too high, I have taken the figures given by these physicists—which, I may observe, up to temperatures of 800° C. are confirmed by Langen.

The equation given by Holborn and Austin for the specific heat of CO_2 at constant pressure is

$$\text{Specific heat} = 0{\cdot}2028 + 0{\cdot}000{,}128{,}4\theta - 0{\cdot}000{,}000{,}05\,\theta^2,$$

θ being the temperature.

The correctness of this equation for temperatures up to 800° C. has been proved, and, assuming that the same equation holds up to 1300° C., the specific heats for each 100° are given in a table in the full paper.

It will be observed from this table, that, although between 0° and 1400° C. there is a large increase in the value of the specific heat, yet the increments per 100° are rapidly decreasing, vanishing altogether at about 1400° C., at which temperature* there would be partial dissociation at atmospheric pressure. The temperature would, however, probably require to be considerably higher at the pressures we are considering.

The specific heats given are, as I have said, those for constant pressure, and to obtain those at constant volume it is necessary to divide by the constant k, connecting the specific heats of gases and vapours at constant pressure and constant volume.

I give the values I have used, (1) of the specific heats at constant pressure—these are taken either from Holborn and Austin's paper, or from Landolt Börnstein, 'Physikalisch-Chemische Tabellen,' 1905; (2) of the constant k—these are all taken from Landolt, pages 407–8; (3) of the specific heats at constant volume.

Gases, etc.	Specific heat, constant pressure.	Value of k.	Specific heat, constant volume.
CO_2	0·2986	1·282	0·232
CO	0·2425	1·401	0·173
H	3·4100	1·408	2·422
CH_4	0·5922	1·316	0·450
N	0·2497	1·410	0·177
H_2O	0·4210	1·330	0·361

The specific heats calculated from the above data, of the gases generated by the explosion of the six propellants, are given in the tables embodying the results of the whole of the experiments for each propellant, and in the tables are also given the temperatures of explosion deduced from Equations (1) and (2), and here again it must be remembered that the temperatures with

* Mendeleef, 'Principles of Chemistry,' vol. 1, p. 381; also Deville, 'Comptes Rendus, vol. 56, p. 729; and Berthelot, 'Comptes Rendus,' vol. 68, p. 1035.

which artillerists are chiefly concerned are those due to densities varying approximately between 0·17 and 0·23.

Beginning with Equation (1), the Italian Ballistite, which shows the highest temperature, commences at the density of 0·05 with 4943° C., this temperature hardly varying at all till the density of 0·25 is reached, when it slowly but regularly increases to about 5000° C. at $d=0·45$. Cordite Mark I commencing at 4742° C. with a very slight fall is practically constant up to $d = 0·30$, after which it rises somewhat rapidly to a temperature of 4921° C. at $d = 0·45$, and to 5065° C. at $d = 0·50$.

When, however, we come to the temperatures given by Equation (2), we are met with some very remarkable differences, which are shown by the tables, but which are more readily appreciated if reference be made to reduced copies of Plates 7, 8, and 9, in which the explosives are arranged in descending order of the temperatures developed.

It will be observed that at the higher densities and pressures, there is generally a very tolerable accordance in the temperatures obtained from the two formulæ, but as the density and pressure diminish, the divergence becomes in all cases considerable, but very greatly more with the explosives which develop very high temperatures, and which give rise to large percentages of carbonic anhydride.

The only construction I am able to put upon the tolerably close approximation of temperature given by the two formulæ at high densities and pressures, and the wide differences which exist in some of the explosives at low densities, is that, as I think it reasonable to expect, at high densities dissociation of the carbonic anhydride is prevented by the very high pressure, and that the great difference between, for instance, Italian Ballistite and Nitrocellulose R.R. at, say, the density of 0·1 is due, firstly, to the difference of the temperature at which the nascent gases are generated, and secondly, to the proportion of CO_2 which is subject to dissociation.

Formula (1) gives for Italian Ballistite at $d = 0·1$ a temperature of nearly 5000° C. (and for this explosive the temperature given by units of heat divided by specific heat is nearly constant), while the percentage of CO_2 is 38·2. The same formula gives for the nitrocellulose at the same density a temperature of formation of 3200° C., while the percentage of CO_2 is only 19·45.

I have pointed out that under atmospheric pressure the dissociation of CO_2 commences at about 1300° C., and the very much higher temperatures of formation of the gases of the Italian Ballistite, combined with its double percentage of CO_2, appear to me to be sufficient to explain the results obtained with this explosive.

If reference be made to fig. VII on Plate 6, it will be seen that while at the

density of 0·1 there is, with Italian Ballistite, a difference of about 1800° C. between the two formulæ, there is with the nitrocellulose a difference only of under 800° C.

The theory I venture to submit is as follows:—

The nascent gases are generated at temperatures approximately as given by Equation (1) and by the upper curve of each explosive in figs. VII, VIII, and IX.

Under the low densities and pressures at the very high temperatures with which we are concerned, the CO_2, and possibly some H_2O, are partially dissociated, giving rise to the fall in temperature exhibited by the results obtained from Equation (2) at low densities. At high densities, as already pointed out, the two equations give, in some cases, accordant results, in all cases tolerable agreement; it therefore appears to me to be reasonable to suppose that the facts I have recorded are due to partial dissociation at low densities and pressures, which dissociation is prevented by the very high pressures ruling at densities of 0·40, 0·45, and 0·50.

As no free oxygen is ever found in the analyses, in cooling down, any free oxygen due to dissociation must have re-combined, and the heat lost by dissociation regained. The re-combination must, however, be very gradual, as no discontinuity is observed in the cooling curves.

It is then pointed out that a certain amount of confirmation is given to the view taken by the fact that if the explosives be arranged according to the amount of heat generated, derived from Equation (1), regard being also had to the amount of CO_2 found, it will be found that the differences between the two formulæ decrease approximately as the factors, to which I have referred, decrease, and a table is given showing these differences.

At the density of 0·45 the differences between the two formulæ are as follows:—

	Difference.
Italian Ballistite.....	150° C.
Cordite Mark I	200
M.D.....	320
Norwegian Ballistite 167	250
Norwegian Ballistite 165	130
Nitrocellulose	180

It will be observed, both from the above figures and the curves, that with the Italian Ballistite alone at the density 0·45 is the temperature derived from Equation (2) lower than that derived from Equation (1). With all the other explosives the temperatures derived from Equation (2) are the higher.

The differences, however, are not great, being generally under 5 per cent., that is, under 200° C.

In the case of experiments carried on both at pressures and temperatures very greatly above the limits at which physicists ordinarily experiment, I can hardly hope that the methods I have employed, and the conclusions at which I have arrived, will escape criticism.

The results of the experiments given in the tables and plates, may, however, be taken as very approximately correct, and the repeat experiments I have made show that there is great constancy in the transformation which takes place on explosion at any given density.

I conclude by expressing my obligation to Dr. Sodeau and Mr. Hutchinson for their assistance in carrying out the various experiments, in the analyses and in the laborious but necessary calculations.

Note.—In the case of the Norwegian Ballistites, the pressures at densities above 0·3 have been corrected to accord with the values obtained from the volume of the gas generated, multiplied by the units of heat determined.

On the "Kew" Scale of Temperature and its Relation to the International Hydrogen Scale.

By J. A. HARKER, D.Sc., Assistant at the National Physical Laboratory.

(Communicated by R. T. Glazebrook, D.Sc., F.R.S. Received June 23,—Read June 28, 1906.)

(From the National Physical Laboratory.)

In October, 1887, the International Committee of Weights and Measures adopted as the standard thermometric scale to which all temperature measurements were to be referred that of the *constant-volume hydrogen thermometer.** When, therefore, thermometric readings are expressed on any other scale the correction to be applied to these to bring them into accord with this standard becomes of importance.

By far the majority of temperature measurements are made by means of mercury thermometers. The ideal mercury thermometer would be one which when subjected to any steady temperature would assume immediately a steady reading identical with that given by the hydrogen thermometer at the same temperature. This ideal is, as might be expected, not attained by any known mercury-in-glass thermometer, and the amount of the departure from the ideal at different temperatures depends on the particular kind of glass employed. So long ago as 1847 Regnault was aware of this fact, and showed that for several of the best thermometric glasses then in use the departure might attain as much as 10° C. above 300° C.

For many years thermometers have been verified at Kew Observatory in large numbers annually, their indications being referred to the *Kew Scale* of temperature. It has recently become a matter of interest to determine to what degree of accuracy the *Kew Scale* may be considered as identical with that of the hydrogen thermometer, and this memoir gives an account of some experiments undertaken at the National Physical Laboratory with a view to elucidate this question.

The only comparisons between Kew thermometers and the gas thermometer of which the author has been able to find a record are those by

* The resolution was as follows :—"That the International Committee of Weights and Measures adopt as the normal thermometric scale for the international service of weights and measures the centigrade scale of the hydrogen thermometer, having as fixed points the temperature of melting ice (0°) and that of the vapour of distilled water in ebullition (100°), under the normal atmospheric pressure; the hydrogen being taken under the manometric initial pressure of 1 metre of mercury, *i.e.*, at 1000/760 = 1·3158 of the atmospheric pressure."

Balfour Stewart,* the observations of Wiebe,† the observations of Guillaume, made at the Bureau International des Poids et Mesures, and the work of Chree.‡

Of these, the first and the last are confined to determinations of the difference between the two scales at the freezing point of mercury. Chree found that at this temperature the mean departure of 20 calibrated Kew standards was 0°·45 F., the mean temperature on the Kew scale being − 38°·35 F., while Balfour Stewart's value for the true temperature on the air scale was − 37°·9 F.

Wiebe's determinations were confined to a single thermometer, which was only divided to ½° C. The composition of the glass of this instrument is given as:—

Silica	44·49	Lime	1·20
Lead oxide	33·90	Magnesia	0·67
Potash	12·26	Alumina and iron oxide..	0·35
Soda	1·54	Manganese oxide	0·13

He compared the instrument directly against an air thermometer between 0° and 100° C. In a *résumé* on mercury thermometry by Schloesser§ the results of Wiebe are given re-calculated as divergences from the hydrogen scale as follows:—

Temp.	Difference. $T_{Eng.\ gl.} - T_{Hyd.}$
10°	+0·008°
20	+0·001
30	+0·017
40	−0·037
50	−0·057
60	−0·073
70	−0·079
80	−0·070
90	−0·046

These numbers are derived from a smoothed curve drawn through the observed values, and take no account of considerable irregularities, which manifested themselves at various points throughout the scale. The fact that the mercury thermometer reads *lower* than the hydrogen over nearly the whole range is pointed out by Wiebe as very unusual.

* 'Phil. Trans.,' 1863, p. 425.

† 'Berliner Sitz.,' 1885, p. 1021; and later, 'Zeit. für Instr.,' vol. 10, p. 435, 1890.

‡ 'Phil. Mag.,' vol. 45, p. 225, 1898.

§ 'Zeit. für Instr.,' vol. 21, p. 296, 1901.

The observations of Guillaume quoted by Benoit* relate to a single English glass standard and appear to have reference to the "movable zero" method. They gave—

Temp.	Difference. $T_{Eng.\ gl.} - T_{Hyd.}$
0° C.	+0·000
10	+0·007
20	+0·005
30	−0·004
40	−0·012
50	−0·021

The usual type of Kew standard thermometer is an instrument having a range from below 32° to above 212° F., and is usually divided only to 1° F. The stems are always of the solid cylindrical type, 5 to 7½ mm. in diameter, and are sometimes with, sometimes without, milk-glass backing. The capillary is always of circular section, and the diameter of the bulb is never greater than that of the stem; but large spherical bulbs were used on some of the oldest specimens. Measurement of a number of representative specimens made at various times over a period of 50 years showed the length of a division (1° F.) varied from 1 to 3 mm., and that the thickness of the division line subtended a length of stem corresponding to from 0°·04 to 0°·08 F. This type of thermometer was intended for work to an accuracy of 0°·1 or 0°·05 F.

For the purpose of this research it was thought desirable, after studying the behaviour of a number of these old thermometers, to construct new standards, having a more open scale and capable of being read to higher accuracy, and to treat these from the beginning in a definite and systematic manner.

The usual type of Kew standard is graduated so as to correct any irregularities in the calibre of the stem, this being effected by making a preliminary calibration of the tube, and appropriately lengthening or shortening the divisions throughout the scale. This is generally successful to the extent that no calibration error exceeding 0°·05 C. persists. Hence the application of a calibration correction is rendered unnecessary.

The readings of a Kew standard are always understood to apply to the thermometer in a vertical position when immersed in water up to the reading, and the instruments are always intended to be used as "fixed" rather than "movable zero" instruments. That is, the normal procedure to measure any temperature on the Kew scale would be to *first* determine the zero and *afterwards* the temperature in question, applying to the latter a

* "Détermination du Rapport du Yard au Mètre," Bur. Int. Poids et Mes., 1896.

constant correction for any deviation of the zero point from its nominal correct value, 0° C., or 32° F., and ignoring all changes of zero produced in the thermometer by exposure to the higher or lower temperature in question.

The increased sensitiveness desired in the new instruments was obtained by constructing them as is now usual for standard work so that the range between boiling and freezing points was spread over two distinct stems. Accordingly, in 1902, 12 thermometers of the solid stem type were blown by Mr. Hicks from glass furnished by Messrs. Powell from their stock, the makers assuring us that it was identical in composition with that supplied for ordinary Kew standards.

The thermometers were annealed very thoroughly according to the following scheme:—On August 19, 1902, they were heated for eight hours to temperatures varying between 260° and 290° C. During this heating the ice-points rose permanently an average of 15 mm. on the scale, *i.e.*, almost exactly 2° C. On August 27 they were again heated for six hours to 250° C., and slowly cooled. There was no further general change of zero point. On September 22 they were heated to 150° C. for 24 hours, and slowly cooled, and in November their fundamental and 50° points were determined.

To permit of the relatively high temperature of this anneal the thermometers were provided with an auxiliary chamber at the top of the stem, in addition to the one always present in Kew standards ranging to the boiling point. This chamber was sufficiently large to contain the necessary mercury to permit of the exposure of the thermometers to a temperature of about 300° C.

Of the 12 thermometers, six were used for this work, all having about the same dimensions and sensitiveness; Nos. 776, 778, and 780 read from below 0° to above 50°, and had the portion between 50° and 100° shortened by substitution of a small bulb for the upper part of the stem between about 52° and 98°. In Nos. 777, 779, and 782 the shortening was between + 2° and 48°, a few degrees of stem being also available above and below the boiling point.*

The table on p. 229 shows their characteristic dimensions. They were all graduated into approximate degrees centigrade by Mr. Foster at Kew, in March, 1903, with the exception of No. 782, which was completed in January, 1905, to replace No. 781 accidentally broken.

* Thermometers Nos. 776 and 777 were only used in the later comparisons, the initial experiments being confined to the other four.

No.	Range.	Nature of stem.	Length of one degree.	Thickness of stem.	Centre of bulb to 0°.	0—50°.	50—100°.
	°C. °C.		mm.	mm.	mm.	mm.	mm.
776	−2 to 51 and 98 to 102	Milk glass	8·05	5·45—5·50	55	402	53
777	−2 „ +1 „ 49 „ 107	„	7·80	5·55—5·60	62	30	365
778	−2 „ 53 „ 97 „ 102	„	7·60	5·75—5·80	60	380	73
779	−2 „ +1 „ 48 „ 105	„	7·40	5·95—6·05	58	44	370
780	−2 „ 52 „ 97 „ 102	Transparent	7·76	5·95—6·00	53	388	71
782	−1 „ +1 „ 48 „ 105	„	7·41	5·90—5·95	53	56	371

Each thermometer was then calibrated with threads of varying length. First a division into two parts was made with four different columns, approximately 50° C.; then a further subdivision of the principal 50° on each stem by two different 10°-columns. This gave with very considerable accuracy the calibration correction for every 10°—the points close to which comparisons were subsequently made. In addition two different 2°-columns were observed with their ends at every even two degrees throughout the scale. From the general mean of the 2°-calibrations perfectly independent values were found for the corrections at 10°, 20°, 30°, 40°, etc. In all cases where the length of the 2°-column was a close approximation to 2°, the results of the two independent calibrations agreed to within the limits of error of such work, and it was always possible to deduce the true calibration correction near the principal points—10°, 20°, 30°, etc.—to within two or three thousandths of a degree.

As in this type of thermometer, owing to the presence of the auxiliary chamber, increments of pressure on the bulb are not directly proportional to increments of temperature, a correction has to be determined to reduce the readings at any point to what it would have been had the point 50° C. been exactly half way between 0° and 100°. For this purpose observations of the 100° point of each of the thermometers were made in the Chappuis steam bath in both horizontal and vertical positions, and from these the pressure coefficient of each thermometer was calculated.

From these observations the following corrections were found for the six thermometers for the point 50° C., giving the amount to be added or subtracted from the reading to make the indications of the instrument comparable with the normal type having a continuous scale from 0° to 100° C. on p. 230.

The thermometers were compared with the standards of the laboratory and one or two other Tonnelot thermometers of French "verre dur," the relation of whose indications to the hydrogen scale had been previously thoroughly

No. of thermometer.	Pressure correction for point 50° C.	Internal pressure coefficient, degrees per millimetre.
776	+0·029	0·0001676
777	−0·029	0·0001762
778	+0·026	0·0001670
779	−0·028	0·0001706
780	+0·036	0·0002259
782	−0·036	0·0002310

studied. Great care was taken to use the Kew standards under the same conditions as they would ordinarily be subjected to at Kew. It is known that the indications of a Kew standard depend on the treatment to which it has been subjected previous to use, and that a thermometer which had often been used over the higher part of its range would not follow the same law as to depression of its zero as one used but seldom.

In order to make strictly consistent the results obtained for the upper and lower parts of the range, got from the two different types of thermometers, in all cases the pairs Nos. 776 and 777, 778 and 779, and 780 and 782 were treated as single instruments, being always taken through precisely similar cycles of temperature change.

Dr. Chree, the Superintendent of the Observatory Department, was good enough to draw up a detailed memorandum as to the methods employed at Kew for their standards used in verification work, and it has been the object throughout this investigation to imitate this practice as closely as possible.

After finishing the calibrations, etc., and determining the zeros, the thermometers were placed in the comparison bath,* which was electrically heated and stirred continuously, and were slowly taken up from the ordinary temperature to the boiling point, the latter being attained in about five hours. The current was shut off after the boiling had continued about half an hour, and the bath was then allowed to cool slowly, with the thermometers in position. This treatment was repeated on three successive days. An interval of one clear day was then allowed, and the comparisons were begun on the following day, an observation of the zero being previously made, and a boiling point determination at the close.

* The bath consisted of two vertical cylindrical vessels, about 20 inches high, connected by horizontal cross tubes near the top and bottom. The whole vessel held about 20 litres of water. The stirring was continuous and very perfect throughout the whole of the larger tube, in which the thermometers were placed. The heating was electrical and could be arranged to give either a stationary temperature or any desired rate of slow rise or fall. It is hoped shortly to publish descriptions, with drawings, of this and other thermometric appliances used at the Laboratory in a special paper.

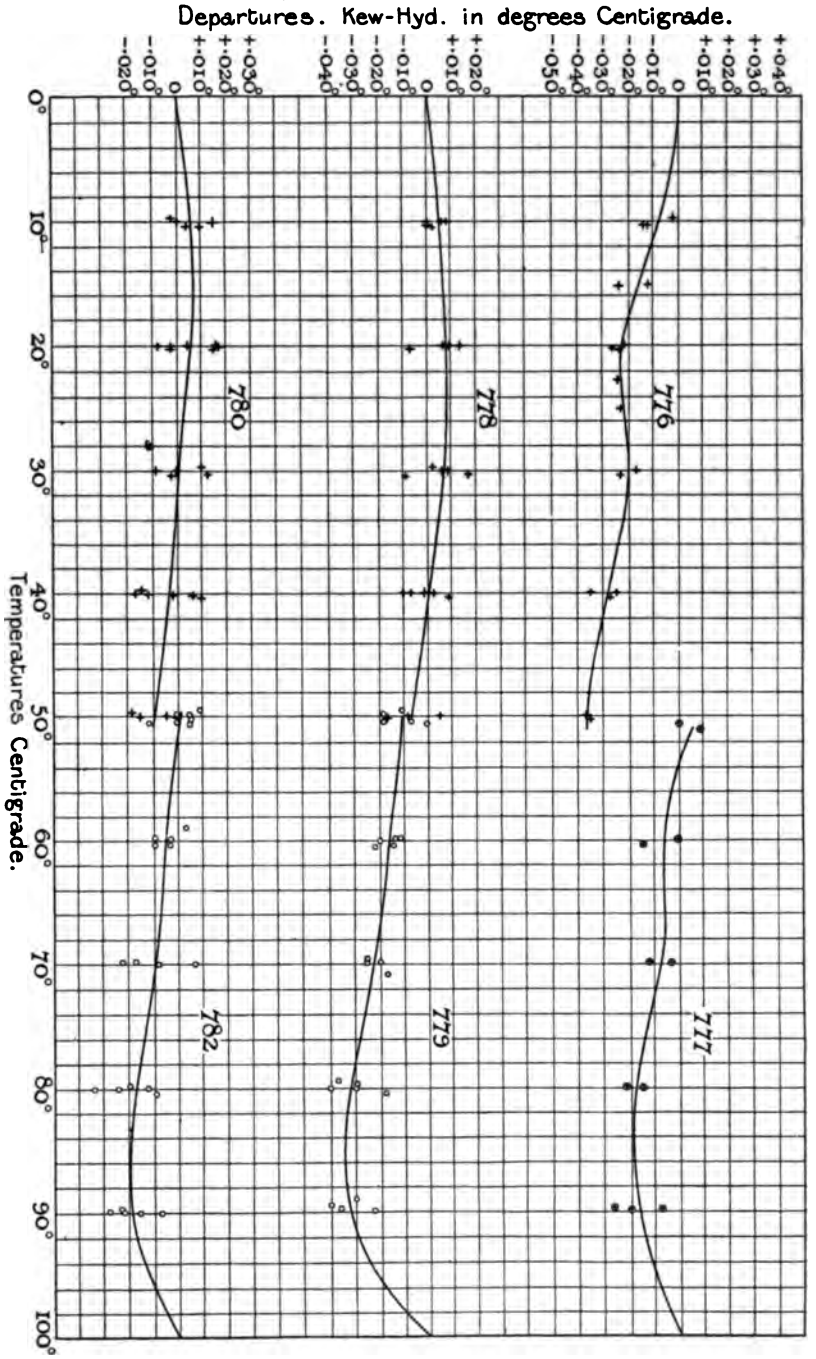
This treatment of heating to the boiling point, and allowing a clear day subsequent to this before commencing the observations, was repeated on each separate occasion, when a complete comparison was made. The sets of observations were made intentionally at intervals of several weeks to test the behaviour over a considerable period.

The following table gives a summary of the observations with thermometers Nos. 778 and 779, the different columns giving the mean values obtained, usually from two, sometimes from four, groups of readings, each group consisting of four observations of very slowly rising temperatures :—

Summary of Comparisons—Thermometers Nos. 778 and 779.

Date.	Zero position before observation.	Temp. on Kew scale.	Temp. on Hydr. scale.	Difference, Kew−hydr.
		No. 778.		
December 1, 1905	−0·044	10·051	10·044	+0·007
		19·853	19·845	+0·008
		29·840	29·838	+0·002
		40·038	40·036	+0·002
		50·061	50·070	−0·009
February 6, 1906.....	−0·020	20·006	20·000	+0·006
		40·048	40·049	−0·001
		49·842	49·849	−0·007
April 30, 1906	−0·036	10·296	10·296	0·000
		10·377	10·375	+0·002
		20·232	20·240	−0·008
		30·389	30·398	−0·009
		40·067	40·077	−0·010
		50·214	50·231	−0·017
May 30, 1906	−0·002	20·052	20·039	+0·013
		30·201	30·184	+0·017
		40·257	40·248	+0·009
		50·089	50·084	+0·005
		No. 779.		
December 1, 1905	+0·015	50·052	50·070	−0·018
		59·945	59·959	−0·014
		69·959	69·979	−0·020
		79·411	79·448	−0·037
		89·060	89·090	−0·030
February 6, 1906.....	+0·027	50·468	50·517	−0·049
		60·423	60·445	−0·022
		80·402	80·420	−0·018
April 30, 1906	+0·003	50·357	50·365	−0·008
		60·317	60·342	−0·015
		69·786	69·811	−0·025
		79·979	80·009	−0·030
		89·805	89·837	−0·032
		89·933	89·956	−0·023
May 30, 1906	+0·031	50·510	50·509	+0·001
		59·887	59·889	−0·012
		69·800	69·825	−0·025
		79·852	79·882	−0·030
		89·573	89·609	−0·036

The concordance of the different observations at any temperature is seen from the accompanying curves, in which all the observations are plotted.



The following example, selected at random from the note-book of observations, shows the order of accuracy of the individual comparisons, etc.:—

Comparisons of February 6, 1906, Thermometers Nos. 778 and 780 with Tonnelot No. 15,504 and Baudin No. 15,959. Zero readings after thermometers had been at room temperature, approximately 10° C., for several days, then for an hour in bath at about 20° C.

Zero corresponding to 20°—

Tonnelot No. 15,504 ...	−0·007	Kew No. 778	−0·020
Baudin No. 15,959	+0·109	Kew No. 780	−0·060

No. 15,504.	Kew No. 780.	Kew No. 778.	No. 15,959.
First set of observations (J. A. H., observer).			
19·852	20·045	19·900	20·020
·870	·060	·910	·025
·900	·080	·950	·060
·920	·100	·955	·060
19·885	20·071	19·929	20·041
Second set of observations (W. H., observer).			
20·120	20·300	20·160	20·280
·140	·310	·170	·290
·155	·330	·190	·325
·165	·350	·195	·325
20·145	20·322	20·179	20·305

For the Kew thermometers the fundamental interval, as got from observations of the steam-point at the close of the day's work, was found—

For No. 778.....	−100·012	Hence F. I. correction...	= −0·012
And for No. 780...	− 99·996	„ „ ...	= +0·004

Reduction of Observations.

	Kew No. 778.	Kew No. 780.		Tonnelot 15,504.	Baudin 15,959.
Reading.....	19·929	20·071	Reading.....	19·885	20·041
Cal. cor.	−0·077	−0·274	Cal. cor.	+0·066	−0·011
Press. cor.....	+0·011	+0·014	Int. press.....	+0·027	+0·031
F. I. cor.	−0·008	+0·001	Ext. „	+0·000	+0·000
Zero cor.	+0·020	+0·060	F. I. cor.	−0·016	+0·000
			Zero cor.	−0·007	−0·109
	19·880	19·872		19·955	19·952
			Hyd.	−0·085	−0·085
				19·870	19·867

Mean hydrogen temperature for first set = 19·869.

	Kew No. 778.	Kew No. 780.		Tonnelot 15,504.	Baudin 15,959.
Reading.....	20·179	20·322	Reading.....	20·145	20·305
Cal. cor.	−0·075	−0·275	Cal. cor.	+0·066	−0·011
Press. cor.....	+0·011	+0·014	Int. press.....	+0·027	+0·031
F. I. cor.	−0·003	+0·000	Ext. „	+0·000	+0·000
Zero cor.	+0·020	+0·060	F. I. cor.	−0·016	+0·000
			Zero cor.	−0·007	−0·109
	20·132	20·121		20·215	20·216
			Hyd.	−0·085	−0·085
				20·130	20·131

Mean hydrogen temperature for second set = 20·131.

	Kew No. 778.	Kew No. 780.	
Mean of two sets	20·006	19·998	Mean hydrogen temperature
Departure from hydrogen	+0·006	−0·002	for mean of both sets = 20·000.

It will be observed that, owing to calibration and zero corrections of considerable magnitude, the readings of the two standards differed at this temperature about 0°·16 C., but when the various corrections were applied in accordance with the usual procedure the concordance between the two thermometers was very satisfactory.

Owing to the fact that four out of the six Kew thermometers have milk-glass back to the stems it is only possible to read them in one position, *i.e.*, divisions at the front, and therefore no elimination of any want of verticality in the bath is possible by the method of turning round the thermometer usually employed in the best work. For the same reason only one position is possible for the zero observations. In the zero bath great attention was paid to the strict alignment of the spring clips holding the thermometer in the ice, but in the comparisons, owing to the surging caused by the stirrer, slight motions of the thermometers were inevitable.

A tilt of 1° from the vertical position would in the Kew thermometers cause a parallax error of about 1/20 mm. or 0°·007 C.

The whole of the observations were plotted on a large scale, a reproduction of which is given in the figure, and from a consideration of the individual values, curves were drawn representing the mean departure of each thermometer from the hydrogen scale throughout its range. From these curves the following values were read off:—

Mean Departure from Hydrogen Scale.

	No. 776.	No. 778.	No. 780.	Mean.	
0	0·000	0·000	0·000	0·000	
10	−0·008	+0·004	+0·006	+0·001	
20	−0·022	+0·007	+0·006	−0·003	
30	−0·020	+0·006	+0·001	−0·004	
40	−0·028	−0·000	−0·003	−0·010	
50	−0·035	−0·008	−0·009	−0·017	
	No. 777.	No. 779.	No. 782.		−0·010
50	0·000	−0·010	−0·000	−0·003	
60	−0·005	−0·015	−0·005	−0·008	
70	−0·010	−0·022	−0·010	−0·014	
80	−0·015	−0·033	−0·018	−0·022	
90	−0·020	−0·032	−0·020	−0·024	
100	0·000	0·000	0·000	0·000	

If the behaviour of the pairs of thermometers were absolutely consistent, the departure from the hydrogen scale of the low-range and high-range types at 50° C. should be identical. The discontinuity is, however, very small except in the case of Nos. 776 and 777. The differences in the last column of the table above are many of them of the same order as the accidental errors of observation in the best work. Thus for example in his "Études sur le thermomètre à gaz" during some elaborate comparisons of the primary standard thermometers Nos. 4428, 4429, 4430 and 4431, on which the "verre dur" scale depends, Chappuis found that in one series at 60° C., No. 4428 read 0°·008 *higher* than the mean of four, and No. 4429 0°·012 lower, while in a second series the positions were reversed, No. 4428 reading 0°·008 *lower* than the mean, and 4429 the same amount *higher*.

In addition to the work on the new special thermometers a systematic comparison was also made of a number of old Kew standards of the ordinary construction divided to whole degrees Fahrenheit. A selection was made of thermometers of widely differing types, which had necessarily been subjected to varying treatment. The zeros of some of them had been displaced appreciably from their original positions. After applying the usual zero-correction to all the observations, but no calibration-interval correction, the results in the table on p. 236 were obtained for the divergence of each from the hydrogen scale.

Of these thermometers No. 560, a high-range thermometer, had a considerable zero error, having been frequently used in the upper part of its scale, and No. 41 was of a somewhat unusual type, and much older than the others, with a transparent stem and spherical bulb. It was formerly the

Old Kew Standards.

Differences Kew—Hyd. (expressed in degrees Centigrade).

No fundamental-interval correction applied.*

	No. 544.	No. 560.	No. 722.	No. 728.	No. 41.	No. 686.
Range	−40° to 215° F.	−10° to 555° F.	−45° to 222° F.	−20° to 122° F.	0° to 220° F. (Spherical bulb, transparent stem)	−20° to 225° F.
Thickness of stem	7·5	7	7	6·5	2·2	7·5
Length of 1° in mm.	2·1	1	1·9	2·7	July, 1852	1·9
Date of completion	September, 1877	June, 1878	July, 1895	March, 1896	—	January, 1889
Maker	T. W. Baker	T. W. Baker	J. Foster	J. Foster		J. Foster
0° C.	+0·00	+0·00	+0·00	+0·00	−0·00	+0·00
10	+0·01	+0·01	+0·01	+0·02	−0·01	+0·02
20	+0·02	+0·02	+0·02	+0·03	−0·01	+0·05
30	+0·02	+0·03	+0·01	+0·03	−0·02	+0·07
40	+0·03	+0·03	+0·02	+0·03	−0·03	+0·10
50	+0·04	+0·04	+0·04	+0·03	−0·06	+0·12
60	+0·04	+0·03	+0·05	+0·02	−0·08	+0·13
70	+0·05	+0·03	+0·06	+0·01	−0·09	+0·14
80	+0·06	+0·05	+0·06	+0·01	−0·08	+0·15
90	+0·06	+0·04	+0·05	+0·01	−0·05	+0·15

* The usual Kew practice would be to apply to any thermometer, new or old, in which a fundamental interval error was observed, as, for example, No. 686 above, the requisite corrections throughout the scale.

property of Mr. G. Griffith, of Harrow, and was obtained for the laboratory by the kindness of Mrs. Griffith in 1904. It will be seen that its scale is almost absolutely identical with that of the thermometer examined by Wiebe.

The above readings apply to the thermometers assuming their fundamental interval to be correct. As, however, the departure from the hydrogen scale is of the opposite sign in the first four instruments to that found in the new standards, it was thought desirable to make measurements of the fundamental intervals of some of them. No. 544 was found to need a fundamental interval correction of $-0°{\cdot}07$, No. 560 of $-0°{\cdot}06$, No. 722 of $-0°{\cdot}03$ and No. 686 of $-0°{\cdot}17$. Applying these to the results in the above table, we have as the *true* departure of the scale of these from the hydrogen scale:—

Old Kew Standards. True Departures from Hydrogen Scale.

Temp. ° C.	No. 544.	No. 560.	No. 722.	No. 686.
0	+0·00	+0·00	+0·00	+0·00
10	+0·00	+0·01	+0·01	+0·00
20	+0·00	+0·01	+0·01	+0·03
30	+0·00	+0·01	+0·00	+0·02
40	+0·00	+0·00	+0·00	+0·03
50	+0·00	+0·01	+0·02	+0·03
60	+0·00	−0·01	+0·03	+0·02
70	+0·00	−0·01	+0·03	+0·02
80	+0·00	−0·00	+0·03	+0·02
90	+0·00	−0·01	+0·02	+0·01
100	+0·00	0·00	+0·00	+0·00

When it is remembered that the length of 1° C. on these thermometers only covers from 2 to 4 mm. and that the divisions are relatively thick, it will be seen that these divergences are wholly negligible, and that within the limits of error attainable all these thermometers used in the normal way by the "fixed zero" method give a close approximation to the hydrogen scale.

Before commencing the first of the normal series of comparisons of the special standards it was deemed to be a matter of considerable interest to make a series of comparisons when the thermometer zeros were in the relatively high position they had attained after the instrument had been a long time at the ordinary temperature. The observations in this set were very complete and extended over two days. Zeros were taken before commencing work, after the comparisons at 50° on the first day, after a second comparison at the same temperature on the second day, and after the steam-points at the conclusion of the observations. From these were obtainable all the data required to calculate the observations, *first* by the ordinary method,

applying the *fixed* zero determined at the commencement, and *second* applying a *depressed* zero calculated by interpolation, from the observations after 10°, 50° and 100°. The fundamental interval correction determined from the steam-point values taken at the finish is, however, notably different in the two systems. Thus, for example, the fundamental interval of No. 778 on the *fixed* zero method is 100°·001, and on the *depressed* 100°·085. The table gives a summary of the differences, Kew—Hyd., obtained by calculating out the same set of values on the two systems.

Summary of Observations calculated by both Methods.

	Temp.	Ordinary method fixed zero after 10°.		Mean departure ordinary method.	Depressed zero method calculated from zeros observed after 10°, 50° and 100°.		Mean departure depressed zero method.
		No. 778.	No. 780.	Kew—Hyd.	No. 778.	No. 780.	Kew—Hyd.
	°						
Sept. 11, 1905	10	+0·008	+0·000	+0·004	0·000	−0·005	−0·002
,,	20	+0·009	−0·008	+0·000	−0·003	−0·006	−0·004
,,	30	+0·009	−0·009	+0·000	−0·006	−0·000	−0·003
,,	40	−0·007	−0·017	−0·005	−0·024	−0·002	−0·013
,,	50	−0·011	−0·036	−0·024	−0·030	−0·013	−0·021
		No. 779.	No. 782.		No. 779.	No. 782.	
,,	50	−0·018	+0·004	−0·007	−0·037	−0·014	−0·025
Sept. 12, 1905	50	−0·019	+0·004	−0·007	−0·001	−0·008	−0·005
,,	50	−0·011	+0·008	−0·002	+0·015	−0·006	−0·004
,,	60	−0·020	+0·002	−0·009	+0·001	−0·008	−0·003
,,	70	−0·017	+0·006	−0·005	−0·002	−0·001	−0·002
,,	80	−0·039	−0·013	−0·026	−0·029	−0·018	−0·024
,,	90	−0·039	−0·007	−0·023	−0·034	−0·009	−0·022

In judging of the results obtained with this series it must be remembered that with thermometers in their virgin state the zero movements are relatively large, and that the time of exposure to any temperature higher than that to which they have been long subjected has a marked influence on the results obtained. A very long period of rest is necessary to completely eliminate the effects of the unavoidable warming of the bulbs in the severing of columns for calibration purposes, and it is not certain that the effect of this warming would be identical in all cases. In so far as can be judged from a single set of observations with the thermometers after lying by for a considerable period, there appears to be almost complete agreement between results of the two methods of using the thermometers, these being in the state when differences would be most likely to be manifested. The results given by

the thermometers do not differ appreciably from what is obtained when in the more normal condition after exposure to varied temperature ranges.

The main conclusions of the work are therefore:—

(1) The departure of the natural scale of the "Kew" mercury-in-glass thermometer from the international hydrogen scale is very small at all temperatures.

(2) For measurement of temperature *differences* over ordinary ranges such as in calorimetry, the results obtained directly or indirectly from a Kew standard may be considered as hydrogen temperatures without application of any correction.

(3) In some instances when defining the temperature at which certain standards have their definite value, such as, for example, the temperature 62° F. for the British standard yard, the temperature scale to which the measurement referred was not definitely specified. This research renders it probable that if the instrument were a good English glass thermometer approximating to a Kew standard, the error made in considering its indications as identical with the hydrogen scale would be within the limits of accuracy of length measurements.

(4) For the ordinary ranges of meteorological and clinical thermometers reading to 0°·1 F., many thousands of which have been verified at Kew annually for many years past, the temperatures as given on the Kew certificate may be considered as hydrogen temperatures.

(5) The table appended gives the mean departure from the hydrogen scale of the "Kew" scale of temperature as observed in this investigation, the figures being rounded to the most probable 0°·005 C. For comparison purposes the figures for French "Verre Dur" and for Jena "Glass 16‴" are added in parallel columns, it being understood that each glass is treated in the manner prescribed for it: the Kew glass being a "fixed zero" scale and the other two "movable zero."

Differences in Degrees Centigrade.

	Kew glass. $T_{Kew}-T_{Hyd.}$	Verre dur. $T_{VD}-T_{Hyd.}$	Jena glass. $T_{16'''}-T_{Hyd.}$
0	+0·000	+0·000	+0·000
10	+0·000	+0·052	+0·056
20	+0·000	+0·085	+0·093
30	−0·005	+0·102	+0·113
40	−0.010	+0·107	+0·120
50	−0·010	+0·103	+0·116
60	−0·010	+0·090	+0·103
70	−0·015	+0·072	+0·083
80	−0·020	+0·050	+0·058
90	−0·025	+0·026	+0·030
100	−0·000	+0·000	+0·000

In conclusion, I must express my indebtedness to the Director of the Laboratory, Dr. Glazebrook, at whose instigation this work was carried out, to Dr. Chree, Superintendent of the Observatory Department, for much valuable information, and to Mr. W. Hugo, who was responsible for the whole of the observational work of the calibrations and also assisted in the comparisons.

Determinations of Wave-length from Spectra obtained at the Total Solar Eclipses of 1900, 1901 *and* 1905.

By Professor F. W. Dyson, F.R.S. (Member of the Expeditions from the Royal Observatory, Greenwich).

(Received April 25,—Read May 17, 1906.)

(Abstract.)

This paper gives the wave-lengths deduced from measures of a number of photographs of the chromosphere and corona obtained in three eclipse expeditions from the Royal Observatory, Greenwich. The spectra extend from wave-length 3300 to 5875.

Nearly all the brighter lines of the chromosphere are identified with practical certainty, the observed wave-length differing in very few cases by 0·1 tenth-metre from the line with which it is identified. The identification was principally made by comparison with the spark spectra of Exner and Haschek, Sir Norman Lockyer's results being used for "enhanced" lines. For comparison, the intensities of the corresponding lines in the spark, arc, and solar spectra are given, obtained from various published sources.

The wave-lengths and intensities of a number of lines in the spectrum of the higher chromosphere obtained at Sfax in 1905 are also given.

The wave-lengths and intensities of the lines observed in the spectra of the corona at the three eclipses are also given.

The paper is purely descriptive and shows in detail the relation between the chromospheric spectrum and those of the spark and arc, but does not attempt to assign physical causes to the differences and resemblances.

An Account of the Pendulum Observations connecting Kew and Greenwich Observatories made in 1903.

By Major G. P. LENOX-CONYNGHAM, R.E.

(Communicated by Dr. R. T. Glazebrook, F.R.S. Received June 22, 1905,—Read June 7, 1906.)

Preliminary and Apparatus.

§ 1. The observations, of which a brief account is here given,* had their origin in the decision of the Government of India to resume the pendulum work which was brought to a close in 1870. Professor F. R. Helmert, Director of the Central Bureau of the International Geodetic Association, to whose advice the India Office is much indebted, recommended the use of a half-seconds pendulum equipment as designed by Colonel von Sterneck. This equipment was ordered through the Geodetic Institute at Potsdam, and the constants for the necessary pressure and temperature corrections were determined there by Professor L. Haasemann, under Professor Helmert's direction. A redetermination of these constants was made at Kew, at Professor Helmert's suggestion, and results were obtained in very close accordance with those found at Potsdam.

The apparatus gives only relative determinations of gravity; it was thus necessary to select a base station. As Kew Observatory ha dbeen the base station of the older Indian pendulum observations it was again selected, Dr. Glazebrook, Director of the National Physical Laboratory, having given permission and promised all necessary assistance. Meantime, a suggestion was made by the Astronomer Royal, and accepted by the Secretary of State for India, that the opportunity should be taken of swinging the pendulums also at Greenwich, thus allowing of a fresh intercomparison of g at Greenwich and Kew.

The apparatus was made by E. Schneider, of Vienna, after Colonel von Sterneck's design. There are four pendulums, Nos. 137, 138, 139, and 140, having times of vibration which are very nearly equal, and slightly in excess of half a second. The pendulums are of brass, heavily gilded, provided with agate edges on which to vibrate. Each carries a small vertical mirror fastened to its head, just above the line of the agate edges. The stand is also of brass, in the form of a truncated cone. It rests on foot screws, which

* The full account will be printed in the publications of the Great Trigonometrical Survey of India.

can be firmly clamped, and carries a highly polished agate plane for the reception of the agate edges of the pendulums.

The pendulum is started swinging with any desired amplitude by means of a lever in the base of the stand. The pendulum swings in air at atmospheric pressure, but is protected from draughts by a cover.

The most essential remaining part of the apparatus is a flash box, containing a contrivance whereby a shutter under the control of a break-circuit clock allows a flash of light to pass through a slit at every beat or alternate beat. This flash is reflected by the mirror on the half-seconds pendulum into a small telescope above the flash box. The times when the flash passes the horizontal wire in the telescope's field correspond to the coincidences of the half-seconds pendulum and the clock. The coincidence interval, c, is connected with the time of vibration, s, of the half-seconds pendulum by the equation

$$s = c/(2c-1).$$

In the present case we have approximately

$$c = 35 \text{ secs.} \quad \text{and} \quad s = 0{\cdot}507 \text{ sec.}$$

The amplitude of swing is observed by means of a scale on the front of the flash box, at a measured distance from the mirror on the half-seconds pendulum. The most convenient initial semi-arc is from 12′ to 15′.

The clock belonging to the apparatus, S.R. 238, was constructed by Messrs. Strasser and Rohde, of Glashütte; its pendulum, made by Riefler, of Munich, is of invar.

Use was also made of the sidereal standard clock at Greenwich, and at Kew of the clock Morrison 8702. Two break-circuit chronometers were also generously lent by Messrs. T. Mercer and Sons and Mr. V. Kullberg at a time when it was feared that S.R. 238 would not be ready for use. The Mercer chronometer was employed during two sets of observations at Kew.

The equipment included thermometers by Messrs. Negretti and Zambra. A barometer and hygrometer were lent by the National Physical Laboratory.

Corrections to Observed Time of Swing.

§ 2. Reduction to a vacuum was made by the formula

$$-\mathrm{K}'(\mathrm{B}+b)\left(1-\frac{3}{8}\frac{e}{\mathrm{B}}\right)\div(760+2{\cdot}79t),$$

where B is the external barometric pressure, e the pressure of aqueous vapour, b any excess of pressure inside the case—all in millimetres of mercury—t the temperature centigrade, and K′ a constant. The values of

K′ for the four pendulums were very nearly equal; the means obtained at Potsdam and Kew were respectively 595×10^{-7} and 605×10^{-7}.

The reduction to 0° C. was made by the formula $-Kt$, the mean values found for K at Potsdam and Kew being respectively $49{\cdot}0 \times 10^{-7}$ and $49{\cdot}4 \times 10^{-7}$. The Potsdam values of K′ and K were employed in the reductions, but the substitution of the Kew values would in no way have modified the conclusions as to the relative values of g at Greenwich and Kew.

The reduction to an infinitely small arc—in all cases a trifling correction—was made by the formula $-s\alpha^2/16$, where s denotes the time of vibration and α the mean semi-arc.

The results were also reduced to an ideal "rigid pillar" by a method used by Kater and developed recently by Professor R. Schumann, of the Prussian Geodetic Institute. Two pendulums vibrating in very nearly equal times are simultaneously suspended from the stand, their planes of vibration being the same. One is suddenly set swinging with considerable amplitude, the other being initially at rest. Observations of the rate at which the second takes up an oscillation from the first supply the means of calculating the small virtual increase in the length of the pendulum, which corresponds to the elastic flexure of the stand and pillar carrying it. The correction thus obtained to the time of swing—the stand being firmly clamped to a granite slab, cemented to a solid masonry pillar about 20 inches high—averaged about -38×10^{-7} second, the mean being nearly the same at Kew and Greenwich.

In the application of the temperature correction mentioned above it is tacitly assumed that the temperature recorded by the thermometer is that simultaneously possessed by the pendulum. In reality, when the change is at all rapid, the mean temperature of the pendulum lags behind that of the thermometer, and a further correction may thus be necessary, which depends on the rate of change of temperature. This "lag" correction was not determined directly for the apparatus in question, but was assumed to be 25×10^{-7} second for a rate of change of 1° C. per hour, that being the result obtained for an almost identical apparatus belonging to the Prussian Geodetic Institute. The mean values of the calculated lag corrections at Greenwich and Kew in the final comparisons were respectively $+0{\cdot}8 \times 10^{-7}$ and $+4{\cdot}4 \times 10^{-7}$ second, temperature always rising during the observations at Kew, and generally at Greenwich. The relative smallness of the correction at Greenwich was due to the temperature being easier to control, the room being larger than that at Kew, and fitted with electric light instead of gas.

Observations and Results.

§ 3. The observations were made as follows, the time of a coincidence being known very approximately in advance. Ten consecutive coincidences were observed; then, after an interval corresponding to 50 coincidences, ten more consecutive coincidences were observed. Ten values of a 60-coincidence interval were thus obtained and their mean taken. After 12 hours the observations were repeated, and a second mean obtained.

Under normal conditions the mean of these two means should be but little influenced by irregularities in the rate of the clock during the 24 hours. The observations were usually made from 9 P.M. to 1 A.M., and from 9 A.M. to 1 P.M. The rate of the clock or chronometer used was derived from star observations at Greenwich. When at Kew, use was made of the Greenwich 10 A.M. and 1 P.M. time signals, any necessary corrections to these being supplied by the Astronomer Royal.

At Kew the pendulums were swung—approximately in the plane of the prime vertical—in the North Room (formerly the platinum thermometer room) of the small house lying to the west of the main building. The position was 100 feet 6 inches west of, 5 inches north of, and 6 feet 4 inches higher than that occupied by Mr. G. R. Putnam in 1900, and by the Kater pendulums swung by Mr. E. G. Constable in 1888. Its coordinates are 51° 28′ 6″ N. Lat., and 0° 18′ 48″ W. Long.; its height above mean sea level 23 feet. At Greenwich the pendulums were swung in the plane of the meridian. The station was the same as that occupied by Colonel von Sterneck, Mr. Putnam, Mr. Hollis, and others. It is in the Record Room, about 20 yards east of the prime meridian. Its coordinates are 51° 28′ 38″ N. Lat, 0° 0′ 1″ E. Long.; its height above mean sea level 155 feet.

§ 4. The first observations were made by Major S. G. Burrard, Mr. E. G. Constable, and Major G. P. Lenox-Conyngham at Kew from June 22 to June 25, 1903, using only the Morrison clock, the Strasser and Rohde clock not having arrived from Germany. On the arrival of the latter clock, it was employed during observations, first at Greenwich, then at Kew, between June 29 and July 9. The results, however, proved discordant on reduction and were rejected, the clock at the makers' request being returned to them to be overhauled. Major Burrard having meantime had to embark for India, the final observations were made by Mr. Constable and Major Lenox-Conyngham. These consisted of observations at Kew from October 14 to October 16 and October 27 to October 31, with intermediate observations at Greenwich from October 20 to October 24. During each 24 hours two observations were made with each pendulum, employing the observatory clock,

and a further two with either the Strasser and Rohde clock or the Mercer chronometer.

Taking the mean of the corrected times of swing from the four pendulums the final result was:—

At Greenwich	0·5067036 sec.
Kew	0·5067001 „

The probable errors in these times were $\pm 3{\cdot}6 \times 10^{-7}$ second at Greenwich and $\pm 3{\cdot}1 \times 10^{-7}$ at Kew.

The mean difference in the times of swing was 35×10^{-7} seconds, and its probable error $\pm 4{\cdot}5 \times 10^{-7}$ second.

The results for the difference in the time of swing from the individual pendulums were as follows:—

Pendulum number	137	138	139	140
(Excess at Greenwich) $\times 10^7$	34	35	36	35

The agreement between the different pendulums is thus remarkably good.

§ 5. For g at Kew the value 981·200 cm. second^{-2} has been accepted by Professor Helmert.* This depends on the preliminary result of the determination of g at Potsdam, viz., 981·274.

If s_1 and s_0 be the times of swing at two stations where g_1 and g_0 are the values of g, then

$$s_1^2 g_1 = s_0^2 g_0,$$

or where $(s_1 - s_0)/s_0$ is small,

$$g_1 = g_0 \{1 - 2(s_1 - s_0)/s_0\}.$$

Hence, assuming the value 981·200 at Kew, and the above-mentioned excess in s at Greenwich, we have at Greenwich

$$g = 981{\cdot}186,$$

with a probable error of $\pm 0{\cdot}002$.

Comparison with Theory.

§ 6. Helmert's formula is

$$g = 978{\cdot}000\,(1 + 0{\cdot}005310 \sin^2\phi)\left\{1 - \frac{2h}{R} + \frac{3h}{2R}\,\frac{\delta}{\Delta} - \frac{3h'}{2R}\,\frac{(\delta - \theta)}{\Delta} + y\right\},$$

where ϕ is the latitude, h the height above sea level, h' the thickness of surface strata of low density, R the earth's mean radius, δ the assumed mean surface density (2·8), θ the actual density of surface strata, Δ the earth's mean density (5·6), y an orographical correction.

* "Bericht über die relativen Messungen der Schwerkraft mit Pendel-Apparaten," 'Report Geodetic Conference of 1900,' p. 321.

The y correction is inappreciable for such flat country as surrounds Kew and Greenwich.

A detailed examination, by Mr. A. Strahan, F.R.S., of the geological evidence as to the surface strata near the two observatories has led him to the following conclusions:—

At Kew there are 1140 feet of strata of average specific gravity 2·06—including 150 feet of London Clay—and 97 feet of limestone, or in all 1237 feet of strata above the palæozoic floor. At Greenwich the London Clay and the limestone are absent, and the estimated depth of the palæozoic floor is 933 feet. The calculated corrections to Helmert's standard value, 978·000 at latitude 0°, are as follows:—

Correction for	At Kew.	At Greenwich.	Difference in corrections. Kew − Greenwich.
Latitude	+3·178	+3·179	−0·001
(h/R) term	−0·002	−0·015	+0·013
δ/Δ „	+0·001	+0·006	−0·005
$(\delta-\theta)/\Delta$ term	−0·011	−0·009	−0·002
Total	+3·166	+3·161	+0·005

Thus the final *theoretical* values are—

Kew ..... 981·166
Greenwich ... 981·161

The observed values are thus, in both cases, slightly in excess of the calculated, and the difference between them is greater than the calculated difference.

Historical Summary.

§ 7. The following table enumerates the differences between g at Kew and Greenwich as found in the present and in previous direct comparisons:—

Year.	Observers.	Method employed.	Kew less Greenwich.
1831 1873	Sabine Heaviside	Seconds pendulums	+0·069
1881	Herschel	Kater's pendulums, Nos. 4 and 6	+0·038
1888	Constable Hollis	Kater's pendulums, Nos. 4, 6, and 11	+0·028
1900	Putnam	Three half-seconds pendulums	+0·012
1903	Burrard Constable Lenox-Conyngham	Four half-seconds pendulums	+0·014

It is satisfactory to note that the results obtained with the modern forms of apparatus agree well with one another and do not differ greatly from the theoretical value. This encourages the hope that henceforth the pendulum may prove as satisfactory in practice as it has always been attractive in theory.

On the Behaviour of Certain Substances at their Critical Temperatures.

By MORRIS W. TRAVERS, D.Sc., F.R.S., and FRANCIS L. USHER.

(Received June 13,—Read June 21, 1906.)

A work entitled "Le Point Critique des Corps Purs" has recently been published by E. Mathias, whose opinion on matters relating to the critical state must always carry weight. In this he discusses at length the various theories which have been put forward to explain certain irregularities observed in the behaviour of substances, which were supposed to be pure, at their critical temperatures. These irregularities are not accounted for by the simpler theories of Andrews and Van der Waals. He calls attention to the experiments of certain investigators, which appear to suggest that the currently-accepted values of the critical constants of many common substances may be vitiated, either owing to the time allowed for the establishment of equilibrium between the coexisting phases near the critical point being insufficient, or the temperature at which the dividing surface vanishes not being independent of the relative masses of the two phases at the temperature at which this takes place.

According to I. Traube, substances contain different kinds of aggregates, which he calls "gasogenic" and "liquidogenic" molecules. It follows that if equilibrium demands that there shall be a certain concentration of these molecules in the vapour and liquid phases respectively, then unless dissociation and association take place instantaneously, there must elapse a time, following any change of condition, before equilibrium can be established between the two phases.

P. de Heen's theory goes further, and, assuming the existence of such complexes, suggests that it is possible that the concentration of them in the two phases is a function not only of the temperature, but also of the relative masses of the two phases, or, in other words, of the mean specific volume of the system under investigation. In this case a system

apparently consisting of a simple substance may be, to take the simplest case, bivariant, instead of being univariant as is usually assumed.

This last theory may, of course, represent a condition either of true or false equilibrium, and in support of the latter supposition certain indirect evidence is forthcoming. Brereton Baker has shown that association and dissociation are delayed and accelerated by the presence of minute traces of certain foreign substances. The dissociation of mercurous chloride, Hg_2Cl_2, into 2HgCl takes place so slowly in the absence of water vapour that the vapour density of the dry substance is almost exactly twice that of the chloride, which has not been so thoroughly dried. It follows that two such samples of mercurous chloride would, at the same temperature, have different vapour pressures, and that if dissociation took place very slowly the intermediate mixtures which would be formed would constitute bivariant systems.

The case in which the velocity of dissociation approaches zero corresponds to that involved in de Heen's theory; Traube's view really involves no new principle. Whether, however, the views of either of them can be realised experimentally is the question which we have now to consider.

The conclusions which have been drawn from the experimental work on which these theories are based have given rise to a distinction between the temperature at which the surface separating the two phases disappears, which is referred to as the temperature of Cagniard-Latour, and that at which the densities of the substance in those parts of the tube formerly occupied by the two phases become equal, which, as in the case of mixtures, is called the critical temperature. That the former is a function of the relative masses of the coexisting phases at the moment of the disappearance of the surface is the first consequence of de Heen's theory, and that the results are markedly influenced by a time factor would follow from Traube's theory. We find, however, that the results of our own experiments in no sense confirm this conclusion, and in fact support the views of S. Young and others, who are opposed to it. We have not investigated the second consequence of the theory, that the densities of the two phases do not become identical at the Cagniard-Latour temperature. However, it appears more than probable that if the first consequence falls to the ground the second will follow it: amongst a considerable amount of experimental evidence in opposition to it, perhaps nothing is more convincing in this respect than Ramsay's simple demonstration of the equality of the densities of the two phases at the temperature of Cagniard-Latour.*

It is worth while quoting some of the experimental results on which

* 'Zeit. Phys. Chem.,' vol. 14, p. 486.

de Heen's and Traube's views are based. The results of Batelli, Zambiasi, Galitzine, and others are given in Mathias' book, but those of the first named will serve as an example. They are as follows:—

Substance.	Date.	Mean specific gravity of substance in tube.	Mean value of Cagniard-Latour temperature.
Alcohol ...	1891	0·3195	236°·59
		0·3448	237·26
		0·3888	235·94
		0·3893	235·67
	1892	0·3439	237·02
		0·4000	236·43
Ether	1891	0·2409	193·60
		0·2767	193·44
		0·2889	193·17
		0·3043	193·01
	1892	0·2520	192·63
		0·3192	192·12

It cannot fail to be noticed that these results do not even show an agreement among themselves. It is common knowledge that it is very difficult to obtain pure dry alcohol, and that only prolonged washing with water will remove the last traces of alcohol from ether. Our first experiments with ether, which had only been washed a few times with water, led to results similar to those obtained by Batelli.

There is, however, another interesting phenomenon which has been observed in connection with those which take place at the critical temperature. It appears that Altschul* was the first to observe that in the case of most liquids there appeared at the critical temperature (Cagniard-Latour), at the level in the tube at which the surface vanished, an opalescent band. His description of the effect is somewhat obscure, and neither from him nor from Wesendonck† have we been able to derive a complete idea of what happens.

As this particular phenomenon appeared to call for further investigation, and as, in spite of much evidence to the contrary, there appeared to exist a doubt as to whether the simple theories of Andrews and Van der Waals were sufficient to account for the changes which take place at the critical temperature, we decided to undertake the experiments which are described in the latter part of this paper. It suffices to state in advance that in making the observations we employed comparatively large masses of the liquids, enclosed in thin-walled glass tubes, and that particular precautions were taken

* 'Zeit. Phys. Chem.,' vol. 11, No. 189, p. 578.

† 'Zeit. Phys. Chem.,' vol. 15, p. 262.

to obtain them pure, and to introduce them into the experimental tubes without contamination. Further, arrangements were made for maintaining a very steady temperature, which could be allowed to rise very slowly towards the critical point.

The Phenomena which Accompany Disappearance of the Surface at the Critical Temperature.

It must be observed in the first instance that the following phenomena take place at a temperature, or are distributed in the same invariable order over a range of temperature, which is dependent only on the nature of the substance under investigation, and that they appear to be absolutely independent of the relative masses of the coexisting phases. That is to say, if we consider any part of the process, such as the disappearance of the dividing surface, we find that so long as the mass of liquid in the tube falls within certain limits, it takes place at a temperature which is constant within the limit of accuracy of the experiments, and in our own experiments to within 0°·05.

If we heat in a glass tube varying masses of a pure liquid, we observe, as we approach the temperature at which the surface of separation vanishes, one or other of the following changes taking place:—

(*a*) The liquid will have completely evaporated before the true critical temperature is reached, and in this case there is insufficient liquid in the tube.

(*b*) The surface will sink towards the bottom of the tube and, at the critical temperature, will disappear at a short distance above it.

(*c*) The surface will neither rise nor fall while the tube is heated through the last small temperature-interval and, at the critical temperature, will disappear about the middle of the tube.

(*d*) The surface will rise and, at the critical temperature, will vanish near the top of the tube.

(*e*) The liquid will fill the tube before the true critical temperature is reached, and if the temperature is raised, the tube will probably burst; in this case there is too much liquid in the tube.

If the conditions described under headings (*b*), (*c*), and (*d*) are produced in tubes of sufficiently large diameter (in the case of our experiments about 1 cm. in diameter and 20 cm. long), the temperature being allowed to rise so slowly that the two phases are brought into equilibrium without ebullition of the liquid phase, the following phenomena will be observed:—

In case (*b*), at a temperature slightly below that at which the surface vanishes, the space below the latter will become opalescent, appearing brown by transmitted light and whitish by reflected light. The effect is not

altogether dissimilar to that produced by the action of an oxidising agent on a solution of sulphuretted hydrogen. The nearer the surface is to the bottom of the tube the more intense is the opalescence. So long as the surface is still visible the effect is limited to the space below it; and though it is fairly evenly distributed throughout that space, it is usually slightly more intense just below the surface. When the surface vanishes, the upper limit to the effect becomes less clearly defined, and if sufficient time is allowed, it becomes diffused throughout the whole tube; the same result may be arrived at by stirring the contents of the tube by means of an iron stirrer operated by a magnet outside the tube.

When the surface disappears there is observed, in the case of sulphur dioxide, evidence of optical discontinuity between the substance in the tube above and below the point at which this takes place; it appears, however, to be merely transient in character, and if it does not vanish without the temperature being raised, it is certainly incapable of existence at a temperature 0°·05 above that of the disappearance of the surface. The opalescence appears to persist over a finite range of temperature; it sets in, in the case of sulphur dioxide, at 0°·1 below that at which the surface vanishes, attains a maximum at about 0°·05 above it, and has completely disappeared at a temperature 0°·1 higher. In the case of ether the effects persist over about 2°.

Under the conditions included under heading (*d*) the position in the tube at which these phenomena make their appearance is exactly reversed. The opalescence *appears above the surface*, and its intensity increases as the latter disappears on approaching the top of the tube.

If, while the tube is being heated through the last small temperature-interval below the temperature at which the surface vanishes, the latter remains stationary, the tube, at the same time, appears slightly and evenly opalescent throughout its whole length. This corresponds to condition (*c*). As we have already stated, the same effect can be produced by stirring the contents of the tube at any moment when the opalescence is observed above or below the surface itself or the point at which it has vanished.

Conditions (*b*) and (*d*) can be reproduced in the following manner. If, when the condition corresponds to (*c*), and the temperature is within the range over which the opalescence is visible, the volume of the space containing the substance is increased or decreased so slowly that the temperature is not lowered or raised appreciably, opalescence will appear below or above the surface itself, or the point at which it vanished, and its intensity will be proportional to the space it occupies.

In the case of some experiments which fall under headings (*b*) or (*d*) it

was observed that when the opalescence first made its appearance it was most intense immediately below or above the surface. This effect was only transitory in character, and it appeared as if the material giving rise to it were rapidly distributed, by convection or diffusion, throughout the phase in which it was formed.

Discussion of these Results.

In the first place, our experiments appear to indicate that liquid vapour (one component) systems in the neighbourhood of the critical point are univariant, as the simple theory demands. If complex molecules of different magnitude exist, equilibrium must be so rapidly established between them and the simple molecules as to negative de Heen's theory, and to render Traube's theory unnecessary. We now pass on to consider the phenomenon of opalescence.

The observations of Altschul and Wesendonck* only extended to the formation of an opalescent band at the point at which the surface between the liquid and vapour vanished at the critical point, and their descriptions convey the impression that the phenomenon is much simpler than appears from our experiments. Bakker's explanation of the effect,† which he attributes to the thickening of the surface layer as the temperature approaches the critical, is based on their work.

It may be pointed out that in tubes of small bore the transient effect, which was described in the last paragraph of the previous section of this paper, may appear to have a prominent character as an opalescent band replacing the dividing surface.

On considering the facts before us we were drawn to the conclusion that there might be a certain resemblance between the systems we were dealing with and those which constitute colloidal, or so-called "pseudo," solutions. The existence of molecular complexes did not appear to be a tenable hypothesis, for reasons which have already been stated; but the optical effects appeared to point to the presence of non-molecular aggregates. Before we proceed further, however, it will be well to consider certain views as to the constitution of colloidal solutions which have been put forward by Donnan,‡ and a suggestion of his with regard to the application of the same theory to the explanation of the appearance of opalescence at the critical temperature.

In dealing with colloidal solutions he combats the view that their

* *Loc. cit.*

† 'Zeit. Phys. Chem.,' vol. 49, p. 609.

‡ 'Zeit. Phys. Chem.,' vol. 46, p. 197.

properties are in any way connected with the existence of very large molecules, and considers the conditions under which "one phase of a system would be distributed throughout the other in a state of very fine division" as constituting a different phase. So far he is, of course, dealing with two component systems, though the nature of the aggregates is not altogether different from those which we shall refer to directly.

At the British Association, in 1904, Donnan put forward a suggestion "for discussion" as to the conditions which were necessary for the existence of such complexes in a liquid-vapour one-component system in the neighbourhood of the critical point. He suggests that at the critical temperature the interfacial tension becomes zero for ordinary values of the radius of curvature, but remains positive for very small values, for which it does not become zero till the critical temperature is passed. Hence we may assume that at temperatures slightly below the critical the interfacial tension is greater for very small radii of curvature than for ordinary curvatures.

Over a range of temperature, including the critical temperature, limited above by the temperature at which the interfacial tension for small radii of curvature becomes zero, and below less sharply, we can imagine that small, non-molecular aggregates, or drops, can be differentiated from either the liquid or vapour phase, and have a stable existence. To such aggregates can we attribute the phenomenon of opalescence; and the range of temperature over which it is observed, and the manner of its appearance and disappearance, are in agreement with the assumptions.

The manner in which such aggregates or drops could be formed lies outside the discussion, but it is possible to arrive at an explanation of the fact that the opalescence is confined to the phase which is decreasing in volume, through movement of the dividing surface, or, at least, is more intense in that phase. Since it is an essential character of the aggregates that they are non-molecular, one cannot imagine them passing from the liquid to the vapour phase by the ordinary process of evaporation, forming for a moment a constituent of the surface layer. Further, the existence of the aggregates assumes that the interfacial tension at their surfaces is greater than that at the surface dividing the liquid and vapour in the tube, of which the radius of curvature is very large. Hence, an aggregate in contact with the surface will not coalesce with it, as would a small "drop" with a larger surface under ordinary conditions. The result would be that, supposing that a certain number of aggregates were formed in either phase, they would remain in that phase so long as they had a concrete existence, and the optical effect to which they would give rise would depend on their dimensions and the number of them in a given space.

Experimental Arrangements.

Method of Maintaining Constant Temperatures.—The apparatus employed was a modification of that described by Ramsay and Young.* The experimental tube was enclosed within a vapour-jacket, which was surrounded by two outer tubes, on one of which a scale was ruled. The top of the jacket was connected with a large air reservoir and a manometer, by means of which the pressure could be measured.

In the experiments with sulphur dioxide the temperatures were determined by reading the pressures and referring to Ramsay and Young's table of vapour-pressures, but as this does not extend to pressures above 800 mm., we determined the temperatures corresponding to the higher pressures by means of a Callendar platinum thermometer for which the constants have already been published.† To avoid possible confusion in the future we set down the following data:—

Vapour-pressure of aniline.	Temperature from platinum thermometer.
772·7	185°
793·4	186
814·8	187
835·9	188
857·6	189
879·8	190
902·0	191
925·0	192
949·0	193
972·9	194

It is interesting to note that though by using aniline we were able to maintain and to recover temperatures constant to nearly 1/50° C., we were quite unable to obtain such good results by employing quinoline, which, boiling under a pressure of about 260 mm., gives a temperature corresponding to that of aniline boiling under a pressure of 960 mm. This is probably due to the fact that the pressure of the vapour in the apparatus is the sum of the vapour-pressures of quinoline and of mercury, the latter being used to cover the rubber stopper which closes the opening at the bottom of the vapour-jacket, and that the saturation of the space inside the apparatus with mercury vapour is not complete. The consequent variations in the temperature will be a function not only of the total saturation pressure of the

* 'Chem. Soc. Journ.,' 1885, vol. 47, p. 640.

† 'Roy. Soc. Proc.,' 1905, vol. 74, p. 528.

mercury vapour at the temperature of the experiment, but also of its relative partial pressure in the mixture.

To guard against accident through the bursting of one of the experimental tubes, the apparatus was enclosed in a cubical box of about one metre on the edge, open at the back, and with an opening covered by a glass plate 2 cm. thick in front. On the two or three occasions on which the experimental tube burst, though the vapour-jacket and guard tubes were shattered, no other damage was done.

Experiments with Ether.

Preparation of Pure Ether and Method of Filling the Experimental Tubes.— The ether was prepared from pure alcohol by the continuous process. About 1½ litres of the liquid was washed with caustic soda solution, and was then shaken 25 times with about its own volume of fresh water to remove alcohol. Rather less than ½ litre of liquid remained; this was allowed to stand for a week in a bottle with excess of calcium chloride, and (after shaking with dilute sodium amalgam to remove traces of ethyl peroxide) was transferred to a flask containing a large quantity of fine potassium wire. After a week the liquid was distilled, and though only the middle fraction was collected, the whole mass appeared to evaporate at a temperature which was constant to within 0°·02 to 0°·03.

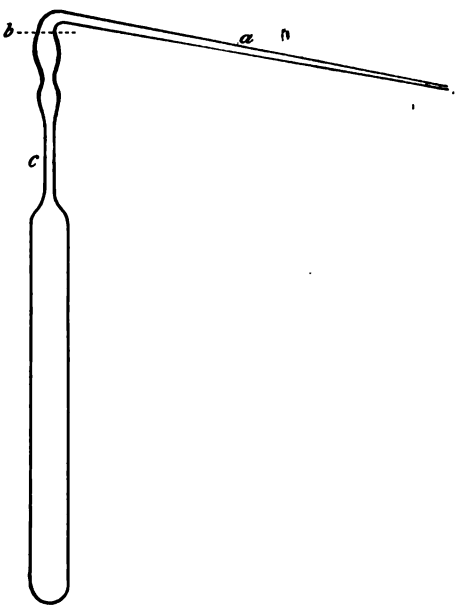


FIG. 1.
(Glass thickened at *c*.)

The experimental tubes, which were of Jena hard glass, were 20 cm. long, 0·8 cm. internal diameter, and 1 mm. thick in the walls, and were made in the form shown in fig. 1. They were first partially filled with ether by dipping the capillary *a* into the ether, and alternately warming and cooling. The tube was then cut off at *b*, the lower end was then cooled in liquid air while the open end was connected by a rubber tube with a Töpler pump. The tube was then completely exhausted, and the exhaustion was continued while the solid melted. When the ether was evaporating freely into the pump the tube was sealed at *c* in a blow-pipe flame.

Details of Experiments with Ether.—Three tubes were used in these experiments. The mean specific volume, that is to say, the volume of the tube divided by the mass of ether contained in it, is given below, the three tubes being referred to by the letters A, B, and C:—

	c.c. per gramme.		c.c. per gramme.		c.c. per gramme.
A	4·10.	B	3·96.	C	3·56.

At the normal temperature, the fraction of the total volume which the liquid occupied was in the three tubes respectively:—

	c.c. per gramme.		c.c. per gramme.		c.c. per gramme.
A	0·35.	B	0·37.	C	0·41.

The following are the details of the experiments:—

Tube and date.	Pressure of aniline vapour.	Temperature, from platinum thermometer.	Remarks.
	mm.		
A 21/3	962·5	193°·57	Temperature falling from above Tc; mist appeared and then liquid, which filled one-fourth of tube; whole tube opalescent. Tube cooled and re-heated.
	963·3	193·60	Temperature rising slowly. Meniscus falling. Whole tube very opalescent, *liquid more so than vapour*. As the meniscus fell, the region *just above it* remained more strongly opalescent than the remainder of the tube. Tube cooled and re-heated.
	963·4	193·60	Meniscus becoming nebulous, and replaced by opalescent band. Point of disappearance less than one-fourth from bottom of tube.
	964·3	193·64	Meniscus quite gone; opalescence very marked, but diffused at point of disappearance. Ultimately opalescence diffused throughout tube. Opalescence persisted for at least two degrees above Tc.
A 22/3	965·4	193·70	At this temperature the meniscus completely vanished, as at 193°·64 on the day before. The behaviour of the ether in the two experiments was identical.
B 22/3	963·0	193·59	Meniscus falling very slightly: liquid occupying about two-fifths of tube.
	963·1	193·59	Meniscus still slowly falling. In this experiment the effects observed were similar to, but less marked than in the case of A.
	963·2	193·60	Meniscus becoming nebulous, and finally disappearing slightly below two-fifths from bottom of tube. The whole tube was then opalescent, particularly at point of disappearance of meniscus.
C 22/3	963·3	193·60	Liquid filling about five-sixths of tube; *vapour much more opalescent than liquid*. Meniscus rising and leaving opalescent band behind it.
	963·6	193·62	Meniscus very close to top of tube, becoming nebulous and disappearing, leaving the whole tube opalescent.

Experiments with Sulphur Dioxide.

Source of the Sulphur Dioxide and Method of Filling the Experimental Tubes.—The substance was obtained in the first instance from a syphon of the commercial liquid. Part of the liquid was allowed to evaporate from the syphon, and then a quantity of it, amounting to about 70 c.c., was introduced into the bulb *a* (fig. 2), which contained excess of phosphorous pentoxide, and which was cooled in a freezing mixture. The stem was then sealed at *b*, the bulb was removed from the mixture, and about a quarter of the liquid in it was allowed to evaporate, so as to remove all traces of air from the apparatus.

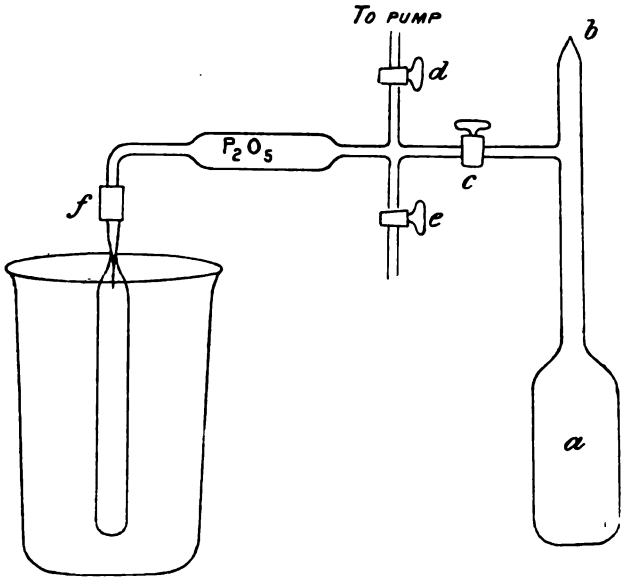


Fig. 2.

The experimental tube was attached by means of rubber pressure tubing at *f*. When it was in position the whole of the apparatus on the left-hand side of the stop-cock *c* could be exhausted through the stop-cock *d*, which was closed while the apparatus was "washed out" with sulphur dioxide and finally filled. During the latter operation the experimental tube was cooled in a freezing mixture; more sulphur dioxide was introduced than it was intended that the tube should eventually contain, the excess being allowed to evaporate into the pump, or to escape into the air through the stop-cock *e*. The tube was finally sealed at the constriction while the pressure in it was still below that of the atmosphere.

It will be observed that we have no direct guarantee of the purity of the

sulphur dioxide. But the results of our experiments on the critical behaviour of successive fractions of the same quantity of liquid indicate that they are at least identical in their properties, and with almost equal certainty that they all consist of one and the same simple substance.

Preliminary Experiments with Sulphur Dioxide.—In the first set of experiments which we wish to record we employed two sealed tubes about 14 cm. long (not counting the length of the capillary portion), and 1 cm. in diameter. The mean specific volumes of the substance in the two tubes, referred to as A and B, were as follows:—

	c.c. per gramme.		c.c. per gramme.
A.....	1·75	B.....	1·67

The tubes were heated as in the case of the experiments with ether in the vapour of aniline, and as the temperatures were deduced by interpolation from the results of Ramsay and Young's experiments, it is not necessary to set down the corresponding pressures. In the following experiments the two tubes were heated together in the same vapour-jacket:—

Temperature.	Remarks on A.	Remarks on B.
° 18	Liquid occupies 0·34 total volume	Liquid occupies 0·40 total volume
156·85	" 0·07 "	" 0·90 "
	As the temperature was raised the liquid in A and the vapour in B became opalescent, the surface in the former rising and in the latter falling. It was noticed that though the temperature could be maintained very constant at any point, equilibrium was only slowly established, some minutes elapsing before the meniscus came to rest and the maximum opalescence was attained.	
157·2	At this temperature the surface in each tube became indistinct, finally disappearing; after some minutes the opalescence vanished.	

Second Series of Experiments with Sulphur Dioxide.—In these experiments arrangements were made for changing the volume of the substance under investigation by means of a compression apparatus, for stirring it by means of a magnetic arrangement during the experiment, and for measuring the temperature of the interior of the tube as well as of the jacket by means of a thermo-electric junction.

The apparatus is shown in section in fig. 3. Into a steel cylinder *b* was screwed a steel tube *a*, about 150 cm. long, connected with another horizontal cylinder into which a piston could be forced by means of a screw, so as to decrease the internal volume of the apparatus, which contained mercury. The experimental tube, which was about 1 cm. in diameter and 50 cm. long, was cemented into the plug *c*, which was screwed into *b*, the

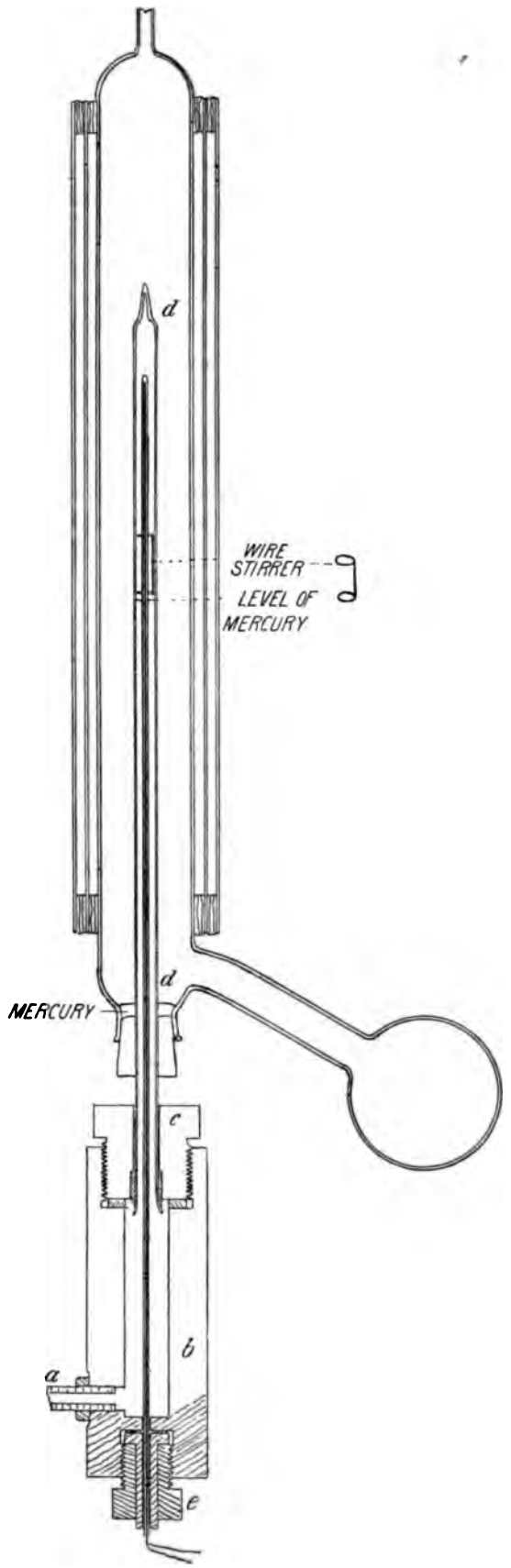


FIG. 3.

Thermo-electric junctions at top and at level of stirrer. At bottom of figure four wires should have been shown.

junction being made good by means of a leather washer. The thermo-electric junctions were enclosed inside a capillary tube of very thin Jena hard glass, which was cemented into a screwed plug *e*, and was so arranged that one junction was at the top of the experimental tube close to the constriction, and another, which was enclosed within the same tube, terminated about 5 cm. lower down. The stirrer consisted of a piece of soft iron wire, bent so as to form two circles a little smaller than the inner diameter of the tube, joined by a straight piece about 2 cm. long, at right angles to them. The stirrer was operated by means of a powerful electro-magnet, the poles of which lay close to the outer guard tube of the vapour-jacket.

The following is a summary of several independent sets of experiments. The measurements of the mean specific volumes of the substance in the experimental tube are only approximate:—

Temperature at which surface vanished.	Mean specific volume of substance.	Remarks.
° ?	2·3	Probably too little liquid in tube.
157·24	2·1	(*a*) When stirred, surface vanished at bottom of tube. No opalescence. (*b*) When not stirred, optical discontinuity at 12 mm. from bottom. No opalescence.
?	2·05	Surface disappeared at bottom of tube.
157·22	2·0	Opalescence at surface, 15 mm. from bottom of tube. On stirring, opalescence was distributed throughout range through which stirrer moved, and optical discontinuity appeared at upper limit of stirring.
?	1·9	As before.
?	1·8	Volume was *reduced* while the temperature was 157°·2, opalescence became very marked, particularly above surface, and diminishing in intensity towards top of tube. Temperature rose to 157°·26; on stirring, optical discontinuity moved to upper limit of stirring, and opalescence distributed itself over the same range.
157·2	1·9	Volume was *increased* while the temperature was 157°·2, when opalescence appeared in liquid, spreading downwards from surface. Maintaining the temperature steady at 157°·2, and the volume constant, the opalescence gradually diffused throughout the tube; after 20 minutes it was impossible to see the window bar through the tube.
157·26	1·75	Tube cooled and volume reduced. On heating to near the critical point the surface now moved slowly upwards, and space above became opalescent. The range of temperature through which the opalescence was visible lay between 157°·15 and 157°·4, over the whole range of volumes investigated.

In measuring temperatures by means of the thermo-electric junction, either of the junctions could be connected by means of a mercury switch with another junction surrounded with the vapour of bromo-benzene, boiling under normal pressure, the free wires being connected directly to the terminals of a

alvanometer. Observations of the pressures under which the aniline in the vapour-jacket surrounding the experimental tube was boiling, allowing ample time for equilibrium to be established, corresponding to certain readings of the barometer, served to calibrate the instrument.

Before filling the experimental tube mercury was introduced into it to a convenient level, a bell-jar was fitted round it by means of a rubber stopper and the latter was filled with a freezing mixture. The capillary portion of the tube was then connected with the apparatus shown in fig. 2, and the correct quantity of sulphur dioxide was introduced in the manner indicated.

Third Series of Experiments with Sulphur Dioxide.—In this series of experiments the same apparatus was used as in the last series, but the thermo-electric junction was omitted, and the temperatures were determined directly from the readings of the pressures. The following are the results:—

Temperature.	Volume occupied by liquid in tube.	Mean specific volume of substance in tube.	Remarks.
157°·0	—	2·03	No opalescence; surface moving downwards.
157·12	0·12	—	Opalescence below surface.
157·3	—	—	„ in lower part of tube; surface vanished, but slight discontinuity visible.
			Volume reduced; tube cooled and re-heated.
157·13	0·68	1·69	Whole tube slightly and evenly opalescent; surface almost stationary with rising temperature.
?	—	—	Surface vanished.
157·3	—	—	Opalescence increased and uniform.
157·4	—	—	„ almost vanished.
			Volume reduced; tube cooled and re-heated.
156·1	0·76	1·55	No opalescence.
157·07	0·79	—	„
157·20	0·88	—	Opalescence above liquid, very strong at surface.
157·3	—	—	Surface vanished, slight discontinuity remaining, with opalescence very strong above it. On stirring, opalescence became diffused throughout tube.
			Volume reduced; tube cooled and re-heated.
157·0	0·95	1·46	No opalescence.
157·15	—	—	Surface nearly at top of tube; minute space above it opalescent.

Note on Opalescence in Fluids near the Critical Temperature.

By Sydney Young, D.Sc., F.R.S., Trinity College, Dublin.

(Received June 18,—Read June 21, 1906.)

The phenomenon of opalescence at and near the critical temperature has been observed by Travers and Usher* under exceptionally favourable conditions, owing to the great width (8 to 10 mm. internal diameter) of the tubes they employed. The opalescence is, however, distinctly visible, and can be studied in much narrower tubes, such as those (0·15 mm. internal diameter) used in my own investigations.

The experiments of Travers and Usher were carried out, for the most part, in such a manner that the total volume of the substance investigated remained constant, while the temperature rose very slowly. In my experiments, on the other hand, the substance was kept at its critical temperature,† and the volume was altered (usually diminished) by equal stages. The opalescence was always seen, but notes of its position and character were only made with a few substances—isopentane and normal pentane, hexane, and octane.

My observations—mostly unpublished—may be regarded as supplementing and, so far as a comparison is possible, confirming those of Travers and Usher, and the following generalisations may be deduced from them:—

1. When observations are made at the critical temperature (Cagniard-Latour temperature) at a series of diminishing volumes, no opalescence is visible so long as the volume exceeds a definite limit. When this limiting volume is passed, a slight opalescence appears at the bottom of the tube, that is to say, just over the mercury; at still smaller volumes the opalescence or mist becomes denser and extends further up the tube. Near the critical volume the mist is very dense, especially near the middle; it may extend all through the tube, or the tube may appear clear either at the top or both at top and bottom. When the volume is further reduced, the mist disappears below, but becomes dense above, and on further compression the clear part extends upwards and the remaining mist at the top becomes less dense and finally disappears at a definite volume.

When observations at the critical temperature are made at a series of increasing volumes, there is a tendency for the mist to be lower down in the tube than when they are made during compression. This tendency may

* *Supra*, p. 249.

† In the case of normal pentane the "Cagniard-Latour temperature" and the "critical temperature" were found to be identical or at least indistinguishable ('Trans. Chem. Soc.,' vol. 71, p. 446, 1897).

probably be explained by the fact that each expansion causes a temporary slight fall below the critical temperature and, consequently, a very slight condensation from the critical to the liquid state (in three cases it was noted that the meniscus was actually seen for a moment). Some little time would be required for equilibrium to be re-established after such a disturbance of the density, and it may be that the time actually allowed—one or two minutes at most—was insufficient. On the other hand, during each compression, there is a very slight rise of temperature, but this does not cause any change of state or disturbance of density.

2. When observations are made at a temperature slightly higher than the critical temperature, the mist is not only much less dense, but the range of volume over which it is visible is more restricted.

3. The limits of volume between which mist is visible at the critical temperature seem to be nearly the same for the four paraffins examined (about 1·17 or 1·18 to about 0·87 or 0·88, taking the critical volume as unity in each case).

One conclusion drawn by Travers and Usher from their experiments is that "the opalescence is confined to that phase which is decreasing in volume through movement of the dividing surface, or, at least, is most intense in that phase." It happens, however, that in their experiments, whenever the liquid phase was small at first, it diminished, and when large at first, it increased; and it may be doubted whether the above relation would be found to hold good for a phase which was large but decreasing in volume, for example, under the following conditions: (*a*) constant volume and slowly falling temperature; (*b*) constant temperature and the total volume either large but decreasing, or small but increasing.

It seems probable from my experiments that the position of maximum opalescence really depends on the mean specific volume of the substance, being near the bottom when the volume is large, near the top when small, and near the middle at intermediate volumes.

This question, although it does not affect the main conclusions arrived at by Travers and Usher, seems to be of sufficient interest to repay further investigation.

The Origin of Osmotic Effects.

By HENRY E. ARMSTRONG, F.R.S.

(Received and read June 14, 1906.)

[*International Catalogue of Scientific Literature.*
Author's title-slip :—C. D.
Subject slips :—
C 0310 A theory of osmotic effects.
C 1930 Association in solution.
C 6250 Association of electrolytes with water.
D 7065 Structure in relation to hydration.
D 7155 Theory of osmotic effects.
D 7255 Explanation of peculiarities of electrolytes.
Q 0224 Origin of osmotic effects.]

The result of the comparative study of enzymes and acids as hydrolysts may be held to be that an explanation *based on an association hypothesis* may be given of their action which is simple and rational and in accordance with the facts. The explanation which has been advocated from the point of view of the ionic dissociation hypothesis, if not inadmissible, is altogether improbable; moreover, whilst this hypothesis is applicable to the explanation of but a very limited class of chemical interactions and is in no way a necessary hypothesis, the assumption that association rather than dissociation is the condition precedent of change* appears to afford a sufficient explanation of chemical interchanges in general, of whatever kind. It is desirable, therefore, to consider somewhat closely what may be the behaviour of salts in solution, in order that their marked activity in comparison with that of non-electrolytes may be accounted for.

It is well known that salts in solution and indeed electrolytes generally produce effects, in lowering the freezing point or the vapour pressure, for example, which are abnormally large in comparison with those which are produced by non-electrolytes. It has therefore been assumed that electrolytes are more or less dissociated in solution into ions which play the part of individual molecules. It is neither desirable to dwell on the inherent improbability of the conception nor to enter into any discussion of the hypothesis, beyond saying that it is difficult to discover any argument of which it is the unavoidable consequence among the reasons put forward in support of its acceptance, as these are inconclusive when not based on uncertain premises; my object is to consider an alternative explanation.

In the case of osmotic phenomena generally, whatever may be the degree

* 'Roy. Soc. Proc.,' 1904, vol. 73, 537; 'Chem. Soc. Trans.,' 1895, 1171.

of fortuitous coincidence between calculated and observed values when they are treated as gaseous pressure effects, the effects cannot in reality be due to pressure in any ordinary sense. In liquids generally attractive forces must come into play between the molecules; in solutions attractive forces must also come into play as between solute and solvent.

It is necessary to account for two classes of facts, viz.:—

1. That non-electrolytes all have a similar influence when used in molecular proportions in solutions of equivalent strength.

2. That electrolytes have an excessive influence as compared with non-electrolytes.

In virtue of 1, it may be supposed that the primary or main osmotic effect is exercised by the solvent—not by the solute. There is apparently no other way in which the constancy of molecular behaviour can be so easily, if at all, accounted for, as the one constituent common to all solutions in a particular liquid is the solvent itself.

In all liquids the molecules must be regarded as in some degree associated. In the case of water it is generally admitted that not only are the molecules associated, but that a relatively large attractive force operates between the molecules—the heat of formation of liquid water at 100° from the fundamental gaseous molecules being a high value ($18 \times 536 = 9648$ calories). The effect of introducing neutral molecules—non-electrolytes—into liquid water must be to cause the dissociation of the molecular complexes to an extent corresponding to the proportion in which the neutral molecules are added. If a substance enter into solution entirely in the form of its fundamental molecules, it will produce its normal effect, provided that its own attractive effect upon the water molecules be inappreciable.

Electrolytes, besides producing the dissociation effect, must be supposed also to exercise an attractive effect on water molecules. In ordinary water, the state of equilibrium involves the simple dissociative change pictured in the equation:

$$(H_2O)_n \rightleftharpoons nH_2O,$$

in which n may have several values, as probably there is a greater number of forms present than two. The introduction of any substance into solution involves the disturbance of the equilibrium in the direction $(H_2O)_n \rightarrow nH_2O$. The osmotic "pressure" is the measure of the extent to which equilibrium is thus disturbed by the liberation of the fundamental molecules or *monads*. These monads are to be regarded as the attracting element in the region of the solution and as conditioning a flow of similar molecules from the region of the pure solvent—or from a more dilute solution—until the two regions are in equilibrium. This explanation was definitely advanced by me in the

'*Encyclopædia Britannica*,' in the article "Chemistry"* published in 1902. The conception has been arrived at from a somewhat different point of view and advocated recently as novel by Mr. Beilby in his Address to Section B of the British Association in South Africa.† Osmotic pressure has been treated as a negative pressure by Hulett‡ and again quite recently by Hudson.§

It may be supposed, in the case of non-electrolytes, that the osmotic attraction is exercised upon external water molecules by the water monads present in excess in the solution as the product of dissociation of the water complexes; in the case of electrolytes, in addition to this attraction, that exercised by the dissolved substance comes also into play: on this hypothesis, electrolytes are substances which are attractive of water practically in proportion to the efficiency of their solutions as electrolytes.

From the point of view here advocated, it is easy to see that, to compare the osmotic efficiency of substances, *it is essential to measure their influence on one and the same proportion of solvent;* the use of *weight-normal solutions*, *i.e.*, of solutions made by dissolving the presumed molecular proportion (or fractions thereof) in a litre of the solvent, as practised by Morse and Frazer,‖ is thus entirely justified.¶ The reason is also clear why only dilute solutions have afforded "normal" results in the hands of the advocates of the dissociation hypothesis and that they have overlooked the important fact discovered by Morse and Frazer, that the osmotic effect varies almost in direct proportion to the concentration, the results obtained with concentrated solutions being, in fact, scarcely less normal than those afforded by dilute solutions.

The presumed distinction between dilute and concentrated solutions almost

* Vol. 26, p. 739.

† [The 'Proceedings' of the Koninklijke Akademie van Wetenschappen Te Amsterdam, of May 26, 1906, issued June 21, contains a communication, by J. J. van Laar, on "The Osmotic Pressure of Solutions of Non-electrolytes in connection with the Deviations from the Laws of Ideal Gases," read on the 29th of April last. Taking Morse and Frazer's observations into account, van Laar arrives at the conclusion that osmotic pressure does not follow the gas laws; he is of opinion that it is "no longer possible to uphold the old conception of the osmotic pressure as arising in consequence of a pressure of the molecules of the *dissolved substance* comparable with the *gas pressure*. The molecules of the dissolved substance have nothing to do with the osmotic pressure except in so far as they reduce the *water* in the solutions to *another state of concentration* (*less concentrated*), which causes the pure water (Concentration 1) to move towards the water in the solution (Concentration $1-x$) in consequence of the impulse of *diffusion*."—*Note added July* 31.]

‡ 'Zeits. Phys. Chem.,' 1903, vol. 42, p. 361.

§ 'Physical Review,' 1906, vol. 22, p. 257 (*re* nature of osmotic pressure; compare Batelli and Stephanini, 'Atti dei Lincei,' 1905 (v), vol. 14, ii, pp. 3--14; also 'Physikalische Zeitschrift,' 1906, vol. 7, p. 190.

‖ 'Amer. Chem. Journ.,' 1905, vol. 34, p. 1.

¶ Compare R. J. Caldwell, *post*, p. 272.

disappears. This is well shown in the following table given by the authors named, in which

N is the proportion of a gramme-molecular weight of sugar which is dissolved in 1000 grammes of water;

D the density of the solution at its freezing point;

Δ the observed depression of the freezing point.

It will be seen that Δ is very nearly 1·85 ND for all concentrations.

N.	D.	$\Delta_1 = 1{\cdot}85$ ND.	Δ.
		°	°
0·10	1·0129	0·187	0·187
0·20	1·0257	0·379	0·373
0·30	1·0380	0·576	0·574
0·40	1·0497	0·777	0·776
0·50	1·0611	0·981	0·970
0·60	1·0717	1·189	1·187
0·70	1·0825	1·401	1·398
0·80	1·0918	1·616	1·612
0·90	1·1016	1·834	1·837
1·00	1·1110	2·060	2·082
1·26806	1·1340	2·660	2·660

It should be pointed out, however, that the fact that "normal" values are obtained in any case must not be taken without further evidence as proof that the molecules present in a solution are essentially of the presumed dimensions. As the presence of associated molecules M_n—*i.e.*, polymorphs of the fundamental molecule or monad M—would condition a smaller effect, whilst the attraction of molecules of the solvent by those of the solute would increase the effect, opposing tendencies may be at work unperceived; especially is this true of electrolytes: the difficulty must always be met with in their case. It follows from this argument that the "normal" effect of a monad cannot be determined in any absolute manner by a purely physical method. Thus the value 1·85 used in calculating the molecular depression of the freezing point, which is based on the observation of the depression produced by alcohol and similar non-electrolytes, is presumably too high, inasmuch as alcohol, in all probability, exercises no inconsiderable attractive effect in solution.

The numbers quoted by Morse and Frazer show in the clearest manner possible that such an effect is at work and that it comes more and more into evidence as the solution is made more and more concentrated. When the values in columns Δ and D in the above table are inspected, it is obvious that whilst the depression of the freezing point becomes greater at an increasing rate, the density increases at a corresponding diminishing rate—the one

compensating the other; to judge from the depression of the freezing point, the attractive forces within the solution become more and more manifest as the concentration increases.*†

At the conclusion of their memoir, Morse and Frazer express the opinion that "some at least of the abnormalities (in the depression of the freezing point) will disappear when the problem is studied from the side of the volume relations of solution and pure solvent": I venture to think that it is already clear that the apparent abnormalities may easily be explained.

Much capital has been made of the additive nature of the properties of electrolytes and of the possibility of assigning specific mobilities to the ions as evidences of their dissociation. But it is forgotten that the properties of many organic compounds which no one dreams of representing as dissociated are additive. My object in referring to this contention here, however, is to lay emphasis on the conclusion which I stated in my paper on "Electrolytic Conduction" presented to the Society in 1886,‡ that hydrogen and the metals generally may be regarded as the analogues of the C_nH_{2n+1} hydrocarbon radicles and that their compounds with negative elements may be likened to unsaturated hydrocarbons of the form $C_nH_{2n+1}.CH:CH_2$. Subsequent study has confirmed this view. I have little hesitation now in stating the opinion that in cases in which they function as simply as carbon

* Compare R. J. Caldwell, *post*, p. 272.

† [In a later paper, which has just been published ('Amer. Chem. Journ.,' July, 1906, vol. 36, p. 39), Morse and Frazer confirm the rule for cane-sugar, $\Delta_1 = 1{\cdot}85\ ND = \Delta$. But it does not hold good, they say, for glucose, the freezing points of glucose solutions being *normal* in the sense that the magnitude of the depression is strictly proportional to the weight-normal concentration. On the other hand, they describe a new series of determinations of the osmotic pressures developed in solutions of cane-sugar, the results of which "are probably as precise as we can hope to obtain under present conditions." They are certainly in remarkable agreement with those calculated on the assumption that "cane-sugar in aqueous solution exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state." They surmise, in order to account for the different results arrived at by the two methods, that at the comparatively high temperatures (20°—25°) at which the osmotic pressures were determined, the whole of the water plays the part of solvent, while at lower temperatures a portion of it is appropriated by the solvent, giving rise to an abnormal depression of the freezing point. Mr. Caldwell's experiments, which were made at 25°, appear to confirm the conclusion arrived at by Lord Berkeley and Mr. Hartley that the osmotic pressures are in excess of the calculated values, although it is true that they worked at 0°. It is difficult to avoid the conclusion that the American observers' values may be too low, perhaps on account of the lack of rigidity in the rubber stopper used in closing the cell. The "normal" behaviour of glucose may be the consequence of the formation of associated molecules compensating the dehydration effect.—*Note added July* 31.]

‡ 'Roy. Soc. Proc.,' vol. 40, p. 268.

does in the paraffinoid compounds generally, metallic atoms are characterised as definitely as the paraffinoid or C_nH_{2n+1} radicles are by specific physical attributes; in the one case as in the other the so-called constants are merely algebraic differences. Variations arise probably only when the metallic atoms become united among themselves by more than single affinities, as in the case of carbon compounds.

But the C_nH_{2n+1} radicle in the compound $C_nH_{2n+1}.CH:CH_2$ is externally inoperative—combination is effected solely through the agency of the $CH:CH_2$ radicle. Applying this argument to metallic salts, the chlorides, for example, the metal may be regarded as inert in solution and the hydration of the salt may be supposed to take place solely through the combination of water with the halogen radicle. In the language of the ionic dissociation hypothesis, only the negative ion is hydrated. Probably, in all its interactions, the activity of a salt is primarily traceable to the negative ion.*

From the electrolytic and osmotic points of view, mercuric chloride, $HgCl_2$, is one of the most remarkable of salts, its behaviour being almost that of a non-electrolyte. It may be contrasted with potassium and calcium chlorides, the former of which has been shown by E. H. Griffiths to depress the freezing point of water at excessively low dilutions to just twice the extent to which it is depressed by the non-electrolyte cane-sugar; the calcium salt has a still greater effect, approaching to three times that produced by the non-electrolyte.

Whilst mercuric chloride dissolves with difficulty in water and is very volatile, it is very readily decomposed into its elements by heat. Sodium and calcium chlorides are easily soluble salts, but neither do they volatilise nor do they decompose when heated, except at very high temperatures. Yet it is confidently argued that potassium and calcium chlorides undergo complete dissociation in solution into free ions, whilst mercuric chloride remains all but unchanged. It is difficult to consider such a contention seriously. In what manner then are the peculiarities of mercuric chloride

* As to the meaning and use of the term ion and its derivatives, it may be pointed out that—pending judgment—no idea of dissociation need nor should be involved in the use of the term. All ions are radicles, but all radicles are not ions: the ion is a radicle which can be moved or separated from a compound by means of an electric current and which is also at once "attackable" under appropriate conditions. For example, the chlorine radicle is present as an ion in sodium chloride, but not in the chlorates nor in chloracetic acid. Used in this way, the term is a most valuable accession to scientific language; it is not until it is coupled with the term dissociation that the radically different conception is introduced about which dispute rages. Faraday applied the term ion simply to "those bodies which can pass to the electrodes": he in no way implied that they enjoyed separate existence in the electrolyte. We may well rest satisfied to use the word in the sense in which he used it.

and similar chlorides to be explained? Conventionally, the three chlorides are represented by the formulæ

$$Hg<^{Cl}_{Cl} \qquad Na—Cl \qquad Ca<^{Cl}_{Cl}$$

But these symbols are equally misleading and inexpressive of their properties. Solid mercuric chloride is probably a weak polymorph, but even its monads must differ in constitution from those of the sodium and calcium haloids. As the mercury haloids all combine readily with other haloids, it cannot be supposed that the halogen is specially exhausted by combining with mercury: therefore, regarding the halogens as potential triads, it may be supposed that in mercuric chloride monads the atoms form a closed system, perhaps thus

$$Hg\langle^{Cl}_{Cl} \quad \text{or} \quad Hg\langle^{Cl-}_{Cl-}$$

Sodium and calcium chlorides, on the other hand, may well be open systems.

$$Na—Cl= \qquad Ca<^{Cl=}_{Cl=}$$

The closed system of the mercury salt is but slightly attractive of molecules of its own kind or of water; the potential activity of the chlorine radicle becomes manifest, however, when the salt is brought into contact with other chlorides which combine with it, forming well-characterised mixed chlorides, *e.g.*,

$$Hg\langle^{Cl}_{Cl} + 2KCl= \quad = \quad Hg\langle^{Cl=ClK}_{Cl=ClK}$$

or it may be

$$Hg\langle^{Cl-}_{Cl-} + 2KCl= \quad = \quad Hg\langle^{Cl—ClK}_{Cl—ClK}$$

Chlorides such as those of potassium and calcium are undoubtedly polymerised in the solid state; when dissolved, the polymorphs undergo simplification at the instance of the water molecules, becoming more or less hydrated. The extent to which depolymerisation and hydration take place depends both on the salt and the degree of dilution; apparently it is only complete in very dilute solutions, judging from the fact that limiting values are only obtained in very dilute solutions.

The formation of hydrates containing several molecules of water may be supposed to involve the association of the salt with water complexes, or it may be that more or less complex ring systems are formed of water

monads corresponding to the ring systems which are so common among organic compounds.

But from the point of view advocated in this note, the complexity of the hydrate would seem to be without influence on the osmotic effect exercised by the salt. To explain the "double effect" produced by potassium chloride monads, it may be supposed that the molecule as a whole has *unit effect*—such as is exercised by molecules generally in freeing water monads—and that, in addition, the chlorine radicle exercises its *proper unit attractive effect.* Other chlorides and salts generally may be expected to exercise an influence in proportion to the number of active "acidic centres." To judge from the behaviour of the sugars and alcohols, it is not improbable that the hydroxyl group may also function as an acidic centre. But inasmuch as chlorides such as mercuric chloride have little or no attractive power for water, it is to be expected that the chlorine radicle or any other equivalent acidic centre will not in all cases exert the full unit effect, but that it will exercise an influence varying from unity to zero, according to the nature of the positive radicle with which it is associated; in other words, the degree of so-called "ionisation" or attackability will vary with the nature of the molecule of which the acidic centre is a component.

Studies of the Processes operative in Solutions. Part I.—*The Sucroclastic Action of Acids as influenced by Salts and Non-Electrolytes.*

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Subject slips :—

C 0310 Hydrolysis of Sugar in relation to.
C 6240 of Acids in presence of Glucose, etc.
D 1820 Cane Sugar, hydrolysis of.
D 7090 Hydrolysis by Acids as affected by Salts.
D 7155 Hydrolysis of Sugar in relation to.
D 7275 Conductivity of Acids in presence of Glucose, etc.
Q 1424 Hydrolysis of Cane Sugar by Acids.]

The investigation of which the results are now recorded is an extension of that undertaken in conjunction with E. Frankland Armstrong in which the sucroclastic action of acids was contrasted with that of enzymes; it forms a necessary part of a larger inquiry which is being carried out at the Central Technical College in the hope of determining the precise nature of enzyme action and of hydrolytic change generally. Evidence was advanced* that the processes must be regarded as similar, notwithstanding the extraordinary difference in activity manifest on comparing the two classes of hydrolytic agents, except that and in so far as third substances produce somewhat different effects, the rate of change being modified in the case of enzymes only by substances which act selectively,† whilst in the case of acids the added substance appeared to exercise an influence which might be regarded as a concentration effect.

It is now obvious, however, that a fallacy underlay our conclusion in so far as the action of acids is concerned and that a like fallacy more or less affects, if it do not invalidate, the conclusions of previous workers in similar fields. It will be clear that to determine the influence of any added substance, this should be made the only variable at first: in point of fact, a second variable—the amount of water present—has also been introduced.

* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 526 ; vol. 74, p. 195.

† *Ibid.*, vol. 73, p. 516.

solutions have been prepared, as a rule, by dissolving the various substances to produce a given volume of solution: the result being that water has been displaced in introducing the third substance. Morse and Frazer appear to have been the first to call attention to the consequences of this practice, in the comprehensive account of their observations on "The Osmotic Pressure and Freezing Points of Solutions of Cane Sugar," published in the July number, 1905, of the 'American Chemical Journal.'* They have shown, at least in the case of cane sugar, that the normal standard volume for osmotic pressure is not that of a gramme-molecular proportion of substance dissolved in water to a volume of 1 litre; the true standard, instead of being such a volume-normal solution, is the weight-normal solution (as they term it) obtained by dissolving a gramme-molecular proportion of the substance in 1 litre of water; such a solution exercises an osmotic pressure approximately equal to the pressure exerted by a gramme-molecular proportion of hydrogen reduced to 1 litre.

The need of maintaining the proportions of water and acid as well as that of the hydrolyte constant throughout the experiments, *so that the amount of the added substance should be the only variable*, was contemplated at the outset of this inquiry; indeed it was undertaken from this point of view at Professor Armstrong's request, before my attention had been directed to Morse and Frazer's communication.†

The experiments now described have shown that cane sugar itself and several other carbohydrates have a relatively small although very distinct concentrating effect; alcohol, however, has a marked inhibiting effect—probably because it enters into competition with the water and withdraws hydrogen chloride from it; glycerol occupies an intermediate position between alcohol and the carbohydrates: in other words, non-electrolytes

* Vol. 34, pp. 28—91.

† In discussing the influence of concentration of the hydrolyte on the rate at which milk sugar is hydrolysed (Armstrong and Caldwell, *op. cit.*, p. 531), results were quoted referring to volume-normal solutions containing 9, 18 and 27 grammes of lactose in 100 c.c. Such solutions contain very different amounts of water, viz. :—

9	grammes	lactose.	91·44	grammes	water.
18	„	„	85·82	„	„
27	„	„	79·96	„	„

The great increase observed in the rate of change is to be attributed mainly to the displacement of water; on reference to Table I it will be seen that the corresponding volume-normal solutions of cane sugar contain a larger proportion of water; the greater influence of changes in concentration on the rate at which milk sugar undergoes hydrolysis in comparison with cane sugar, referred to in the paper under consideration (p. 531), is probably more apparent than real, but the subject is one which needs further experimental investigation.

have comparatively little influence in promoting hydrolysis. The weak electrolyte acetic acid also has but little influence. Metallic salts accelerate the rate of change, the influence of those derived from monad metals being already considerable and that of salts derived from dyads at least twice as great; it will be contended that their activity is due to their dehydrating influence.

The literature relating to the action of acids on cane sugar is extraordinarily voluminous, at least 140 papers having been published which bear on the subject. As the writer is engaged in preparing for the British Association a report summarising the work which has been done, it will be unnecessary to consider at length the arguments which have been advanced. Ostwald, besides carrying out a series of observations on the action of a variety of acids on cane sugar, which led him to conclude that the activity of the several acids was of the same order as that established by other methods, especially by the determination of their electrical conductivity, also made a few experiments on the influence of the concentration of the sugar on the rate of hydrolysis. The results he obtained led him to infer, in the case of chlorhydric acid, that the amount of sugar hydrolysed in unit time increased rapidly, out of all proportion to the increase in the concentration of the sugar. On altering the concentration of the acid, maintaining that of the sugar constant, he noticed a similar lack of proportionality between the rate of inversion and the amount of acid present, the acid being less active in dilute than in strong solution: according to his method of stating the case, whereas the molecular conductivity of the acid diminishes as its concentration is increased, its molecular sucroclastic activity increases as it is increased in concentration. Ostwald was inclined to attribute the lack of parallelism to secondary effects, especially to the accelerating influence of the sugar, which became greater the larger the proportion of sugar present relatively to acid. Water was left out of account.

In his memoir on the velocity of the inversion of cane sugar by acids, published in 1889, Arrhenius introduced the conception of an active mass and attributed the invertive power of acids to the free hydrogen ions; this conclusion has been somewhat fully considered in the paper by E. F. Armstrong and Caldwell, in which also reference was made to his later views published in 1899. It is noteworthy that in his "Allgemeine Chemie," published in 1889, Ostwald expressed the opinion that an acid inverts sugar because of the predisposing affinity of the acid for the alcoholic hydroxyls of the dextrose and levulose produced from the cane sugar. He appears, however, to have been at once converted by Arrhenius.

In 1897 it was contended by Cohen that the great increase in velocity in

more concentrated solutions might be explained by assuming that, as in the case of gases, the space occupied by the molecules would be of consequence; he supposed the rate of inversion to be inversely proportional to the space at the disposal of the molecules.

In all cases, the method of treatment adopted by previous workers has been influenced, in the first place, by the prevailing practice of dealing with volume-normal solutions in laboratory work; and subsequently by the conception introduced by Van't Hoff that the state of the molecules of a substance in solution may be regarded as analogous to that of the molecules in a gas; *the fact being overlooked that as the concentration is varied the proportion of water present is also varied.* No attempt has been made to evaluate the chemical influence of the omitted water.

The extent to which the two methods of treatment afford different results will be at once apparent on reference to the upper half of the Diagram representing the results which I have obtained in a series of experiments—carried out in the manner described towards the close of this paper—which are summarised in Tables I, II and III.

When sugar and acid are dissolved together in water to a constant volume, solutions are obtained which undergo inversion at a rapidly increasing rate the more concentrated they are, the rate being an approximately linear function of the concentration (Equation 1, p. 288). When weight-normal solutions are used, no such rapid acceleration is observed, the rate being but slightly greater in concentrated solutions as compared with dilute solutions. In the former case, the weight of water present diminishes rapidly as that of the sugar is increased, practically following a linear law (Equation 2): the proportion of water, therefore, is varied both with reference to the sugar and to the acid. In the latter case, apart from changes in the bulk of the solution, only the sugar is varied, water and acid remaining constant.

No useful conclusion as to the nature of the processes operative in concentrated solutions can be drawn from the experiments carried out with volume-normal solutions until the results are reduced to weight-normal terms.

The results of a series of determinations of the electrical conductivity (molecular) of hydrogen chloride in presence of varying amounts of glucose are recorded in Tables IV, V and VI; the results when 1 gramme-molecular proportion of hydrogen chloride was present are also represented in the lower half of the Diagram. It will be seen that the difference is but small, due to the use, on the one hand of volume-normal solutions, on the other of weight-normal solutions; but this arises from the fact that the molecular conductivity of hydrogen chloride changes only to a slight extent on dilution. It should perhaps be pointed out that glucose was used in these experiments

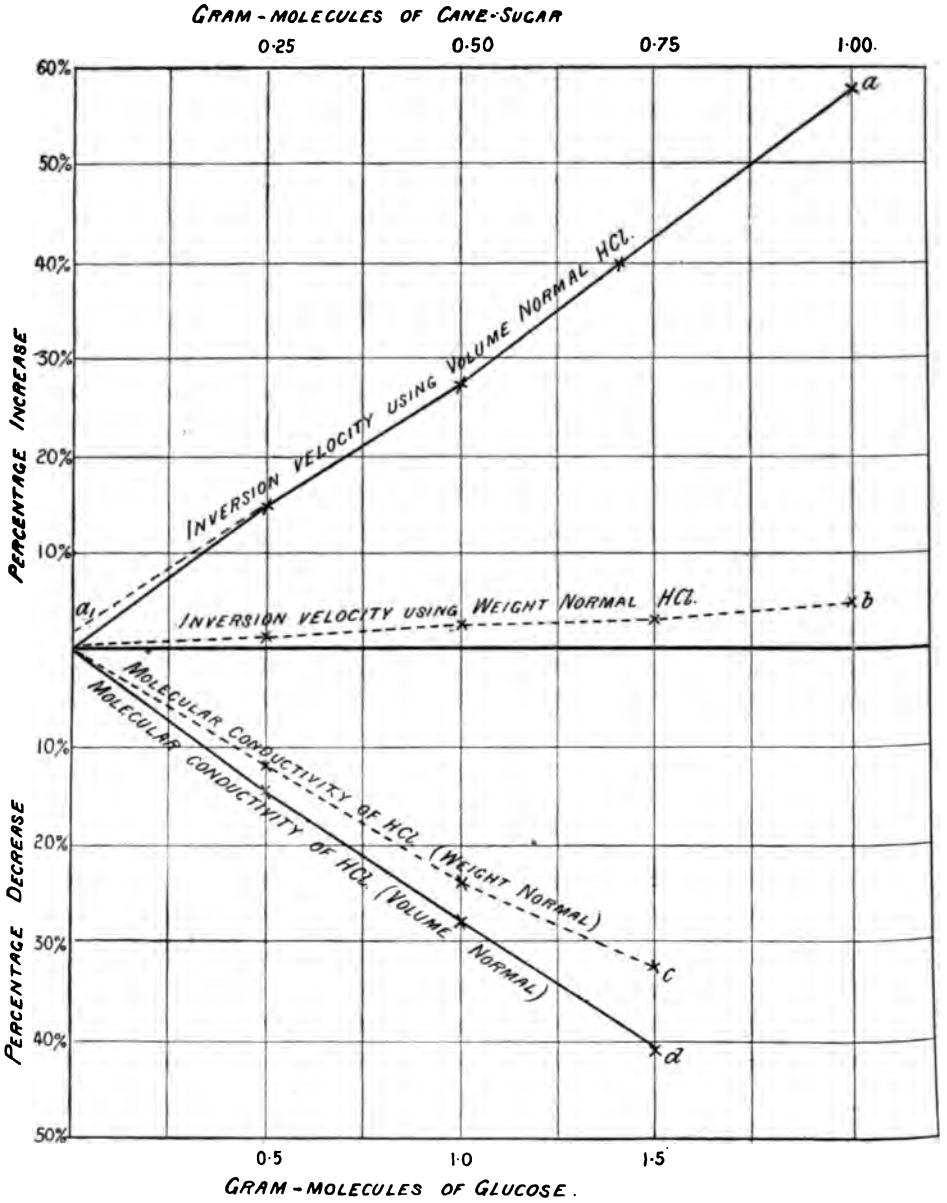

DIAGRAM.

The value obtained (490, Table III) by exterpolating the volume-normal curve on the assumption that the rate is a linear function of the concentration is, doubtless, somewhat low: hence the irregular character of the curve a. If the more probable value deduced from weight-normal solutions be taken as the origin (498), the curve becomes less irregular, as in curve a_1.

n place of cane sugar (*cf.* p. 280), as being its practical equivalent, in order o avoid the complications introduced by the changes attending inversion.

The fact that the effect of increasing the amount of the sugar is to increase he invertive power of the acid whilst it diminishes its conductivity is a trong argument against the application of the ionic hypothesis to hydrolysis, specially when taken in conjunction with the argument previously published n contrasting the hydrolytic activity of acids with that of enzymes.

The results of experiments which I have made to ascertain the influence of dded substances on the rate of hydrolysis of cane sugar by an aqueous olution of chlorhydric acid are summarised in Table VII. The substances used were as follows:—

Lactose, Glucose, Glycerol, Alcohol, Potassium chloride, Ammonium chloride, Barium chloride, Calcium chloride, Sodium chloride, Acetic acid.

It will be seen that all these substances, excepting alcohol, have a more or less marked accelerating effect when used in volume-normal solutions, under conditions, that is to say, which involve more or less water being displaced by the added substance; when weight-normal solutions are used, glucose and lactose appear to have practically no effect, whilst glycerol and alcohol retard the change, all the remaining substances accelerating it.

In view of the general character of the effect produced by salts, bearing in mind also that easily soluble, hygroscopic salts, such as calcium chloride, have a far greater influence than sodium chloride, for example, it appears justifiable to regard the acceleration as a *concentration effect* due to the withdrawal by the dissolved substance of a certain proportion of the water molecules, which thus become removed from the sphere of action of the acid. To evaluate this effect I have determined the number of gramme-molecules of water which must be used in addition to the 1000 grammes originally taken, in order that the rate of change may be that characteristic of the solution prior to the addition of the "neutral" substance. These values are given in the last column of Table VII and are printed in thick type.

The explanations given by previous observers of the effects produced by added substances on the hydrolytic activity of acids have been of a varied character, but with scarcely an exception unsatisfactory and wholly biassed by ionic conceptions. Arrhenius* uniformly resorts to his idea of an "active part," which is either reduced or increased in amount to suit the conditions of the problem. Löwenthal and Lenssen,† who were the first to notice the accelerating effect of salts, attributed their action to the fixation of water and the consequent concentration of acid: hitherto, no one has accepted this explanation.

* 'Zeits. Phys. Chem.,' 1889, vol. 4, p. 226; 1899, vol. 28, p. 317.

† 'Journ. Prakt. Chem.,' 1862 (i), vol. 85, pp. 321 and 401.

To repeat the statement made in a previous paper*: "A very simple explanation of the action of acids may be given if the problem be considered from a point of view similar to that applied to enzyme action. In the first place, it may be assumed that *an active system* is formed by combination of part of the sugar with part of the acid—and as the water molecules in the solution are attracting both sugar and acid molecules, that there is, so to speak, competition between the water and the sugar for the acid; there will be, therefore, at any given temperature, an equilibrium between water, sugar and acid, depending on the relative proportions of these three constituents; a change in any one of them will necessarily also change the position of the equilibrium and therefore also the proportion of the combination of acid and sugar present."

Influence of Concentration on the Hydrolysis of Cane Sugar.—If the change be of this kind, in order to explain the gradual increase in the rate at which the cane sugar is hydrolysed as the solution is concentrated, it is necessary to consider the influence which an increase in the number of molecules of sugar present might exercise. From the point of view of the increased opportunity afforded to the acid, the rate of change should be proportional to the amount of sugar present; but if it be supposed that the sugar or indeed any substance present in the water is to some extent associated with the solvent, any increase in the amount of dissolved substance must involve a corresponding increase in the concentration of the substances participating in the interchange† and therefore must increase the rate of hydrolysis. Actually, this is what occurs. The observed increase in the rate cannot, however, be regarded as the absolute measure of the extent of the dehydrating influence of the sugar, as some portion of the latter may be present as an associated and, therefore, probably less active, if not inert, form.

In view of the presumed connection between osmotic pressure and rate of change, it may be pointed out here that, although the osmotic pressures

* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 533.

† As it is probable that the molecules are not all equally hydrated in solution, the sugar molecules themselves may be less hydrated in a more concentrated solution: it may be that the less hydrated or anhydrous molecules are the more open to attack by the acid. Perhaps this assumption might account for the effect of high pressures on the inversion velocity, which effect has hitherto failed to receive a satisfactory explanation. Röntgen ('Wied. Ann.,' 1892, vol. 45, p. 98), Stern ('Ann. Phys. Chem.,' 1898, vol. 59, p. 652) and Rothmund ('Zeits. Phys. Chem.,' 1896, vol. 20, p. 168) have independently recorded the fact that a high pressure decreases the inversion velocity to the extent of 1 per cent. per 100 atmospheres, although both the "ionisation" and the "ionic mobility" are increased. It may well be that the degree of hydration of the sugar is increased by pressure and that under a high pressure the sugar, being more highly hydrated, would be less open to attack and the inversion slower in consequence.

determined by Morse and Frazer* in weight-normal solutions of cane sugar do not differ appreciably from the calculated values, the results which Lord Berkeley and Mr. Hartley† have brought before the Society recently, when calculated on a similar basis, appear to be somewhat above the calculated values, especially in the case of the more concentrated solutions.

My observations appear to afford considerable support to the results arrived at by the English observers. On the other hand, taken in conjunction with my results, the conclusion at which they have arrived may be held to elevate the assumption that the sugar molecules are hydrated almost to the level of certainty.

Influence of Alcohol.—A single molecular proportion of alcohol per litre, in a volume-normal solution, is *apparently* without influence; inasmuch, however, as it displaces almost its own volume of water in the solution, it must be held to have a considerable retarding effect. That this is the case is seen on reference to the result obtained in weight-normal solution, the value being reduced from K = 510 to K = 467.

Using larger proportions of alcohol, previous observers‡ have noticed a retarding effect even in volume-normal solutions; the explanations which have been offered of its influence are in no way satisfactory. In certain cases alcohol has been shown to have a marked accelerating effect, as in the formation of urea from ammonium cyanate.§

Alcohol may be pictured as acting in at least three ways:—(1) Mechanically, by its interposition between the acting substances; (2) as exercising a concentrating effect such as the sugars exercise by combining with water; (3) as entering into association with the active agent, viz., hydrogen chloride, forming an "alcoholate." Of these (1) and (3) would be unfavourable, whilst (2) would accelerate the change. There is every reason to suppose that all three influences are operative and that the concentrating effect of alcohol is more than counterbalanced by the extent to which it interferes mechanically and (probably) more especially by the formation of an alcoholate.

Influence of Glycerol.—Although apparently, in volume-normal solution, glycerol has a slight accelerating influence, the effect is more than accounted for by the amount of water which it displaces. Considered from the rational standpoint, *i.e.*, in weight-normal solutions, it has a distinct retarding effect, which is considerably less, however, than that of alcohol. The arguments

* 'Amer. Chem. Journ.,' 1905, vol. 34, p. 1.

† 'Roy. Soc. Proc.,' 1906, A. vol. 77, p. 156.

‡ Compare Kablukow and Zacconi, 'Journ. Russ. Chem. Soc.,' 1891, vol. 23, p. 546; Wakeman, 'Zeits. Phys. Chem.,' 1893, vol. 11, p. 49; Cohen, *ibid.*, 1898, vol. 25, p. 1; Arrhenius, *ibid.*, 1899, vol. 28, p. 317.

§ Walker and Kay, 'Chem. Soc. Trans.,' 1897, vol. 71, p. 489.

used in respect of alcohol are also applicable to glycerol; it may again be supposed that the retardation is mainly due to a withdrawal of some part of the hydrogen chloride in loose combination with the alcohol. The readiness with which glycerol is attacked by acids is in harmony with this explanation.

Influence of Glucose.—A series of experiments, the results of which are not quoted, showed that in volume-normal solution the effect of a single gramme-molecular proportion of the allied substances glucose, galactose and mannitol is practically identical. Moreover, glucose can be substituted for cane sugar almost weight for weight in volume-normal solutions without sensible change in the rate at which the cane sugar is hydrolysed, whatever the proportions present. But inasmuch as glucose displaces slightly more water than cane sugar the results obtained with weight-normal solutions are slightly lower in presence of glucose. Thus, the constant K is lowered from 521, the value given by a gramme-molecular proportion of cane sugar, to 518 by substituting for half the cane sugar a gramme-molecule of glucose.

Seeing that the glucose must interfere mechanically, the glucose must be supposed to be at least as highly hydrated as the approximately equal weight of cane sugar. There is no reason to suppose that it will differ much from the cane sugar in its affinity for the acid.

It is very noteworthy that in all cases the constant K has practically the same value throughout the course of an experiment (*vide* Tables X and XI). Hence it follows that whatever changes take place in the solution the influence exercised by the products of change must be almost exactly equal to that exercised by the sugar originally present which undergoes hydrolysis in accordance with the equation :—

$$C_{12}H_{22}O_{11} + OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6},$$

It is obvious that the argument already used with reference to glucose will apply equally well to fructose; and inasmuch as the two molecules of hexose are even superior in dehydrating power to a single molecule of cane sugar, it would seem to follow that most, if not all, of the oxygen atoms exercise an influence on water molecules.

Bearing in mind the complex nature of the influences at work, it is altogether remarkable that the simple monomolecular law should be found to hold throughout;* this result may serve to show how very necessary it is to exercise caution in judging from apparently simple results as to the true nature of the underlying phenomena. It may be expected that more concentrated solutions will give results showing an *increase* in velocity as the hydrolysis proceeds, owing to the fact that the proportion of water which

* *Vide* Mellor and Bradshaw, 'Zeits. Phys. Chem.,' 1904, vol. 48, p. 353.

enters into combination will be a sufficiently important fraction of the total water present to influence the rate. Experiments to test this conclusion are in progress.

Influence of Lactose (Milk Sugar).—In volume-normal solution the addition of half a molecular proportion of lactose* to the same amount of cane sugar, although it gives rise to the displacement of slightly more water, has actually less effect than the cane sugar; in other words, lactose is less effective as a dehydrating agent than cane sugar. This conclusion is in harmony with the recognised character of the substance, especially its moderate solubility, which may be regarded as an indication of a tendency to form relatively inert, associated molecules.

In weight-normal solutions it is apparently without effect; in other words, it exercises a dehydrating influence which is only sufficient to balance the small reduction in activity brought about by its mechanical interference.

Influence of Acetic Acid.—As this acid has practically no hydrolytic effect on cane sugar in comparison with the effect of chlorhydric acid, it is possible to determine its influence as a "neutral" substance. It will be seen that it exercises a slight concentrating effect equivalent to the withdrawal of a single molecule of water by each molecule of acetic acid. This is entirely in accordance with its known behaviour as a weak dehydrant.

Influence of Salts.—Salts have uniformly a concentrating effect; the addition of a molecular proportion of calcium chloride to a volume-normal solution more than doubles the rate of change.

To determine the "degree of hydration" of the salt, the extent to which it was necessary to dilute the weight-normal solutions in order to reduce the value of the constant K to 510—the standard value—was determined in each case. The values arrived at are as follows:—

$NH_4Cl\ 10H_2O$ $KCl\ 10H_2O$ $NaCl\ 13H_2O$

$BaCl_2\ 19H_2O$ $CaCl_2\ 22H_2O$

These values are necessarily somewhat low, as no allowance can be made for the mechanical interference of the salt. They are clearly rational values, however; moreover, they are in accordance with estimates arrived at in other ways.

The results obtained by H. C. Jones and his colleagues,† although con-

* No exception to the use of lactose in this connection can be taken on the ground that it would be attacked by the acid and thus give rise to complications. Under the conditions of the experiments, no appreciable hydrolysis of lactose occurs during 24 hours. (*Vide* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 530.)

† 'Amer. Chem. Journ.,' 1904, vol. 32, p. 310; 1905, vol. 33, p. 548; 1906, vol. 35, p. 445.

firmatory of the values now arrived at in the case of calcium chloride and probably also of barium chloride, are not in harmony with them in respect of other substances. The literature on the subject is so voluminous that it cannot be discussed in an adequate manner on the present occasion; but it may be pointed out that the method described in this communication is one which involves only the consideration of the effect produced on the cane sugar, whereby a measure is secured (in the case of salts) of the concentration effect from which the average degree of hydration of the salt is inferred without reference to the condition of this salt in solution. The method of calculation adopted by H. C. Jones, however, is one which does not in itself permit of any line being drawn between effects produced on the one hand by hydration and on the other by polymerisation.

From this point of view, it may be noticed on comparing the degree of hydration of potassium and sodium chlorides and of barium and calcium chlorides that the more soluble salt of each pair is more hydrated. It is probable that in most cases the less soluble salt is present in solution to the greater extent in a polymerised form.

It is scarcely necessary to add that the values given in Table VII apply only to the particular degree of concentration which was studied. It may be expected that in more dilute solutions the "degree of hydration" would be greater, whilst in more concentrated solutions it would be less.

The limits of variation in the case of sodium chloride are relatively small, as shown in Table VIII, in which is given the average degree of molecular hydration in solutions containing from 1 to .5 gramme-molecular proportions of salt.

Conductivity as Influenced by the Presence of Non-electrolytes.

The equations given in Table IX represent the results obtained in a series of experiments which were made with the object of ascertaining the influence of various carbohydrates on the electrolytic conductivity of solutions of hydrogen chloride and of sulphuric acid, with a view of ascertaining in what way the condition of the acid might be influenced. The effect is in all cases of the same order, equal weights having practically the same effect in lowering the conductivity.

Down to N/8 strength the proportional influence of the dissolved substance is independent of the concentration of the acid; at high dilutions ($v = 128$) as shown in Tables XII to XV, the added substance produces a greater proportionate effect than in the more concentrated solutions.

In all probability the effect of the added substance is mainly mechanical

in the more dilute solutions, however, the non-electrolyte apparently has a distinct dehydrating effect on the acid.

Experiments are being carried out to determine the influence of chlorides on the conductivity of hydrogen chloride, in order to ascertain whether their influence may not also be regarded in the light of the view put forward in this communication. This is the more desirable, inasmuch as it is clear that the influence of salts on the hydrolysis of cane sugar by acids is incompatible with the view which is commonly held that a neutral salt diminishes the extent to which the acid undergoes electrolytic dissociation in solution.

Experimental.

Materials Used.—An approximately twice normal solution of pure hydrogen chloride was used, which was standardised by titration with baryta against a solution prepared by Moody's absolute method;* the conductivity of the acid was determined from time to time in order to ascertain whether any alteration had taken place. A few measurements were made with sulphuric acid which had been standardised by Marshall's method.†

The purest obtainable centrifugalised crystals of cane sugar were used; this material did not reduce Fehling's solution.

The milk sugar was crystallised from 50 per cent. alcohol; the conductivity of a solution containing $\frac{1}{2}$ gramme-molecule of the sugar dissolved in one litre of water was 0·000030 reciprocal ohms.

Kahlbaum's purified glucose, mannitol and galactose were used; these were all tested by the conductivity method. In determining the conductivity of these carbohydrates, a difficulty arises from the fact that, in presence of the platinum black of the electrodes, they are slowly oxidised, giving products which are better electrolytes. It was, therefore, necessary to determine the conductivity at different intervals of time and to exterpolate, to determine the conductivity at the moment of putting the solution into the measuring cell. The conductivity of solutions of one gramme molecular proportion of each sugar in a litre of solution determined in this manner was, in the case of glucose, 0·000043 reciprocal ohms, in that of mannitol 0·000046 and in that of galactose 0·000064 reciprocal ohms. On account of the relatively high conductivity, it was suspected that galactose contained some alkaline impurity, especially as it was found to produce an abnormally large diminution in the conductivity of N/128 hydrochloric acid. To purify it, 80 grammes were dissolved in 60 c.c. of water by heating the mixture;

* 'Chem. Soc. Trans.,' 1898, vol. 73, p. 658.

† 'Soc. Chem. Ind.,' 1899, vol. 18, p. 4.

200 c.c. of methyl alcohol were then added to the cooled solution, and carbon dioxide was bubbled into the liquid, which was subsequently filtered and allowed to crystallise; the latter process occupied a considerable time. The galactose was washed with methyl alcohol and dried during two weeks *in vacuo* over potash. In this manner the conductivity of the gramme-molecular solution was reduced to 0·000035 reciprocal ohms.

The salts used were recrystallised until neutral, excepting the calcium chloride, which contained a little free alkali; this salt was always carefully neutralised with the predetermined amount of centinormal chlorhydric acid before starting the inversion.

Temperature.—The temperature gradient for the inversion of cane sugar is so large that it is important that the temperature should be very carefully regulated. The inversion experiments were carried out in a polarimeter tube which was maintained at 25° by a stream of water from a thermostat. The arrangements are depicted in fig. 1. Water taken from a low-pressure main

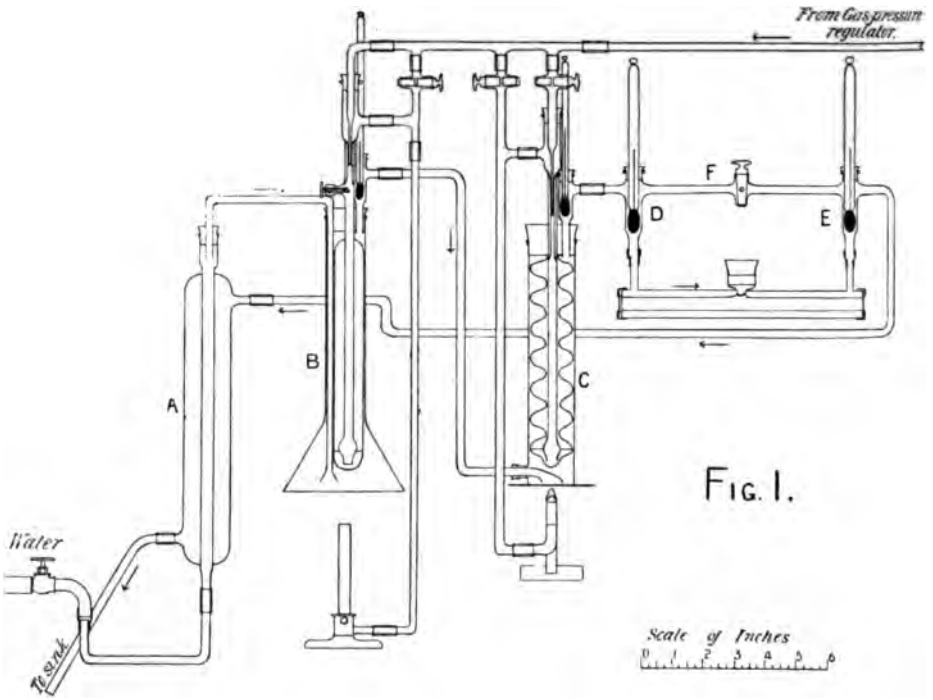

FIG. 1.

at a temperature varying between 10° and 18° was first passed through a condenser A in which it was warmed by the waste water returning from the polarimeter tube. Thence it passed to the bottom of the funnel-shaped vessel B, made of sheet copper, which contained a rough toluene thermo-

regulator in connection with a bunsen flame beneath the vessel; the stream of water was heated to an approximately constant temperature of 24° in this vessel. It then passed into the bottom of the cylindrical vessel C, also made of sheet copper and flanged at the bottom; this vessel is almost filled by a sensitive toluene thermo-regulator with fluted sides; a small flame beneath the vessel in connection with the regulator served to heat the stream of water to a constant temperature of 25°. The water thus heated passed through the small chamber D containing a sensitive thermometer and thence directly into the jacket of the polarimeter tube. The temperature of the waste water was also read in E. When the polarimeter tube was removed, the stream of water could be diverted through the tube F. In order to reduce the loss of heat to a minimum, the vessels A, B, C, D and E and also the polarimeter tube were packed round with felt. The whole apparatus was placed in a room kept at a constant temperature of 20° (at the level of the polarimeter) by means of a gas stove controlled by a large thermo-regulator shaped like a gridiron and filled with saturated solution of calcium chloride.

The temperature of the liquid in the polarimeter tube was found to oscillate 0°·02 C. on each side of the mean temperature, 25°·00 C., in regular periods of about 1·4 minutes. In experiments which extend over an hour, this small variation is of no importance. The drop in temperature of the stream whilst passing through the jacket was negligible.

The conductivities were determined in a large thermostat maintained at 25° C. by means of the spiral toluene thermo-regulator described by Lowry.* It was found to be of advantage to use a gas-pressure regulator with the former thermostat; a very simple and satisfactory device for this purpose is shown in fig. 2. The gas is introduced from the main by tube *a* and passes over the surface of the mercury in the cup *b*, which is firmly fixed to the inner bell-jar by a glass rod *c*; this rod is continued upwards and slides in the fixed tube *d*, which serves as a guide for the floating bell-jar. The pressure of the gas escaping through *e* is that given by the difference in level between the water inside and outside the floating jar and is arranged to be less than the minimum pressure of the gas in the mains. When this regulator is at work the inner bell-jar is in a state of continuous vibration: the gas is therefore passed into a Winchester quart bottle which serves as a buffer; it escapes as a stream of gas at the steady constant pressure indicated by the gauge glass *f*.

Method of Making the Inversion Experiments.—The exact quantity of sugar required together with any additional substance was weighed out for each experiment. The solids were then carefully transferred to a weighed 50-c.c.

* 'Chem. Soc. Trans.,' 1905, vol. 87, p. 1030.

standard flask with water of low conductivity and dissolved in about 24 c.c. by heating the liquid to the boiling point. After cooling, the exact amount of twice normal chlorhydric acid (25 c.c.) was run in from a standard burette and the whole made up to 50 c.c. at 25°. The flask and its contents were then weighed again, in order that the weight of water in a litre of solution could be calculated. When a weight-normal solution was required, a 50-c.c. flask was used which had a bulb blown on the neck above the graduation mark. The exact amount of water could then be run in from a burette to make the total up to 50 grammes of water after the 50 c.c. of solution had been weighed The well-mixed solutions were then filtered directly into the polarimeter tube at 25° C. and allowed at least 10 minutes to attain to the temperature of the thermostat before taking the first reading. Rotations were then taken—15 in all, in each experiment—at 30, 35, 40—100 minutes after the first and the final reading after 24 hours, by which time the rotation had reached its minimum. Each of the recorded rotations is the mean of five readings taken at minute and half-minute intervals on each side of the mean time. The 65 hydrolyses herein recorded thus represent over 5500 polarimeter readings. The error in the value of the constant for each experiment is certainly very small, as will be obvious on reference to Tables X and XI, which are entirely representative of the results obtained in each separate experiment; on this account, it is thought to be unnecessary to reproduce more than four complete sets of the observed values as specimens of the actual course of the experiments. In cases in which the results are not in close accordance, the discrepancy should be attributed rather to differences in the preparation of the solutions than to errors in the determination of the velocity.

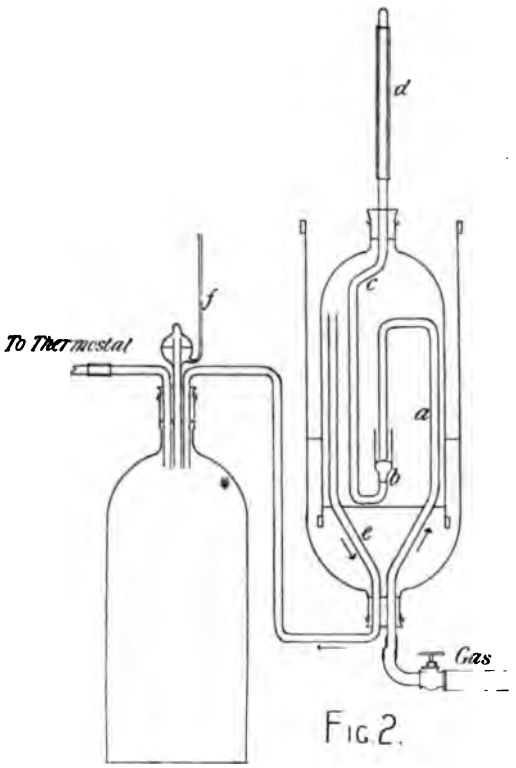

FIG. 2.

Conductivity Measurements.—The measurements of conductivity recorded in Tables IV, V, XII, XIII, XIV and XV were made in a U-tube resistance cell of the ordinary type, using the Kohlrausch wheel bridge, inductorium and telephone. It was found to be of advantage to insert a liquid rheostat in the telephone circuit, which had no influence on the reading but enabled the noise in the receiver to be altered at will, thus securing greater accuracy.

In all cases the calculation was of the following type :—

N/8 chlorhydric acid.	18 grammes glucose in 1000 grammes water =1116·8 c.c.
Resistance of coils	100·0 ohms.
Reading of bridge-wire	536·6 „
Resistance	115·84 „
Less resistance of leads	0·09 „
Resistance of cell	115·75 „
Specific conductivity	0·03250
Less conductivity of glucose	0·000043
Less „ water	0·000003
Conductivity of N/8 HCl	0·032454

The values given in the tables are multiplied by 1000.

The measurements with N/128 acids were made in a cell of the 'Arrhenius' type.

Table I.—Inversion Velocities, using 1 gramme-molecule of Hydrogen Chloride.

Gramme-molecules of cane sugar.	Volume of solution = 1 litre.			Solution in 1000 grammes of water.		
	Velocity constant.	Mean K.	Weight of water.	Velocity constant.	Mean K.	Volume of solution.
			grammes.			c.c.
0·25 (85·5 grammes)	557 563	560	929·4	504 504	504	1069·4
0·5 (171 grammes)	624 621	622	876·7	508 512	510	1122·6
0·75 (256·5 grammes)	696 699	698	824·4	514 512	513	1175·4
1·0 (342 grammes)	768 772	770	771·8	520 522	521	1228·2

Table II.—Inversion Velocities and Weights of Water per Litre of Solution, using 1 gramme-molecule of hydrogen chloride and varying the amount of cane sugar in 1 litre.

Gramme-molecules of cane sugar.	Mean velocity constant.	Calculated velocity constant. (Equation 1.)	Mean weight of water.	Calculated weight of water. (Equation 2.)
			grammes.	grammes.
0·25	560	560	929·4	930·6
0·5	622	630	876·7	877·4
0·75	698	700	824·4	824·6
1·0	770	770	771·8	771·8

Equation 1—

$$K_m = 490\ (1+0{\cdot}5714\ m)\ \text{grammes},$$

Equation 2—

$$\text{Water per litre} = (1000-17{\cdot}1-211{\cdot}1\ m)\ \text{grammes};$$

where K_m is the inversion velocity for a solution of m gramme-molecule of cane sugar per litre.

Table III.—Relative Rates of Inversion by Hydrogen Chloride of various Concentrations of Cane Sugar in Volume-normal and Weight-normal Solutions.

Gramme-molecules of cane sugar.	Volume-normal.		Weight-normal.	
	Velocity constant.	Relative velocity constant.	Velocity constant.	Relative velocity constant.
1·00	770	1·571	521	1·046
0·75	697	1·422	513	1·030
0·50	622	1·269	510	1·024
0·25	560	1·143	504	1·012
—	Calc. (490)	1·000	Calc. (498)	1·000

Table IV.

Conductivity of Chlorhydric Acid in presence of Glucose (volume-normal).

Glucose in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.				
	1.	2.	4.	8.	128.
270	193·3	105·2	55·09	28·32	—
180	235·8	127·7	67·09	34·50	2·266
90	280·0	152·2	79·93	41·17	2·736
0	327·9	178·3	93·61	48·22	3·211

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No glucose.	1·5 gramme-molecule glucose per litre.			1 gramme-molecule glucose per litre.			0·5 gramme-molecule glucose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327·9	193·3	193·3	—	235·8	235·1	0·7	280·0	280·0	—
2	356·6	210·4	210·2	0·2	255·4	255·7	−0·3	304·4	304·5	−0·1
4	374·4	220·4	220·7	−0·3	268·4	268·4	—	319·7	319·7	—
8	385·8	226·6	227·4	−0·8	276·0	276·6	−0·6	329·4	329·4	—
128	411·0	—	—	—	290·0	294·7	−4·7	350·2	350·9	−0·7

$$C_m = C_0(1-0{\cdot}3017m+0{\cdot}01865m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the glucose per litre.

Table V.—Conductivity of Chlorhydric Acid in presence of Glucose (weight-normal).

Glucose in grammes per kilogramme of water.	Dilution of acid in kilogrammes of water per gramme-molecule of HCl.			
	1.	2.	4.	8.
27	184·8	99·25	52·18	26·79
18	221·4	120·7	62·94	32·45
9	265·9	147·0	76·18	39·48
—	320·8	178·9	93·21	48·23

Molecular Conductivities (weight-normal).

Glucose in grammes per kilogramme of water.	Dilution in kilogrammes of water per gramme-molecule of HCl.			
	1.	2.	4.	8.
27	220·2	234·8	245·8	251·9
18	251·2	271·3	281·5	290·1
9	286·7	313·9	324·3	334·9
—	327·4	362·2	375·7	389·9

$$C_m = C_0(1-0{\cdot}290m+0{\cdot}0445m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of glucose per kilogramme of water.

Table VI.—The Relative Electrical Conductivities in presence of varying Amounts of Glucose of Chlorhydric Acid in Volume-normal and Weight-normal Solutions of Hydrogen Chloride.

Gramme-molecules of glucose.	Volume-normal.		Weight-normal.	
	Molecular conductivity.	Relative conductivity.	Molecular conductivity.	Relative conductivity.
1·5	193·3	0·590	220·2	0·673
1·0	235·8	0·719	251·2	0·767
0·5	280·0	0·854	286·7	0·876
—	327·9	1·000	327·4	1·000

Table VII.—Inversion Velocities, using 0·5 gramme-molecule of Cane Sugar, 1 gramme-molecule of Hydrogen Chloride and 1 gramme-molecule of added Material (unless otherwise stated).

Added substance.	Volume of solution = 1 litre.		Solution in 1000 grammes of water.		Solution in 1000 grammes + X gramme-molecules of water.	
	K.	Weight of water.	K.	Volume of solution.	K.	X.
		grammes.		c.c.		
—	624	877·4	508	1122·6		
—	621		512			
Glucose (½ gramme-molecule)	694	820·3	515	1179·7		
	698		514			
Glucose (1 gramme-molecule)	—	—	517	1242·8		
			519			
Glycerol	654	801·0	485	1198·4		
Alcohol	623	818·8	467	1182·4		
Lactose (½ gramme-molecule)	725	767·6	510	1233·2	494	$1H_2O$
KCl	906	845·8	671	1154·2	539	$8H_2O$
	897		682		538	
					521	$9H_2O$
					508	**$10H_2O$**
NH_4Cl	907	833·4	666	1167·0	521	$9H_2O$
					510	**$10H_2O$**
NaCl	963	858·6	738	1141·4	**507**	**$13H_2O$**
	963		725		**509**	
$BaCl_2$	—	—	—	1164·2	468	$22H_2O$
					496	$20H_2O$
					495	
					507	**$19H_2O$**
$CaCl_2$	1313	844·1	980	1156·1	626	$15H_2O$
			983		**511**	**$22H_2O$**
					511	
$CH_3.COOH$	692	821·2	521	1179·6	**507**	**$1H_2O$**

ıble VIII.—Inversion Velocities, using 0·5 gramme-molecule of Cane Sugar, 1 gramme-molecule of Hydrogen Chloride and 1000 grammes of Water, together with a variable number of gramme-molecules of additional Water and of Sodium Chloride.

Gramme-molecules of NaCl.	Gramme-molecules of additional water.	Total volume of solution.	K.	Average hydrate of NaCl.
		c.c.		
1	—	1141·4	738	
			725	
	13	1375·4	507	
			509	$NaCl\ 13H_2O$
3	33	1786·4	513	$NaCl\ 11H_2O$
	36	1840·2	486	
5	25	1687·8	917	
	45	2040·2	561	
	48	2093·8	515	$NaCl\ 9{\cdot}6H_2O$

ıble IX.—Equations representing the Influence of Carbohydrates on the Conductivity of Chlorhydric and Sulphuric Acids of Concentration varying between 1 gramme-molecule and $\frac{1}{8}$ gramme-molecule per litre (volume-normal).

Chlorhydric Acid.

Glucose ..... $C_m = C_0(1-0{\cdot}3017m+0{\cdot}01865m^2)$.
Galactose ..... $C_m = C_0(1-0{\cdot}2902m+0{\cdot}0148m^2)$.
Mannitol ..... $C_m = C_0(1-0{\cdot}2902m+0{\cdot}0101m^2)$.
Milk sugar..... $C_m = C_0(1-0{\cdot}5563m+0{\cdot}0768m^2)$.

Sulphuric Acid.

Glucose ..... $C_m = C_0(1-0{\cdot}2927m+0{\cdot}0077m^2)$.

C_m represents the conductivity of a solution of acid containing m gramme-olecules of added sugar in a litre of solution.

Table X.—Inversion Experiments at 25° C. with 1 gramme-molecule of HCl.

Time in minutes.	Solution contains— 1 gramme-molecule of cane sugar + 772·1 grammes of water in 1 litre.		Solution contains— 1 gramme-molecule of cane sugar + 1000 grammes of water in 1228·2 c.c.	
	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.
	° ′		° ′	
0	32 7	—	30 47	—
30	12 44	766	17 57	519
35	10 27	763	16 16	518
40	8 11	768	14 38	518
45	6 6	774	13 5	519
50	4 13	777	11 36	520
55	2 38	774	10 16	519
60	1 7	775	8 57	521
65	−0 14	773	7 46	520
70	−1 31	774	6 37	520
75	−2 38	772	5 36	519
80	−3 40	771	4 30	522
85	−4 40	773	3 34	521
90	−5 33	773	2 42	520
95	−6 22	773	1 49	522
100	−7 3	770	1 3	521
∞	−15 4	—	−11 47	—
	Mean	772	Mean	520

Table XI.—Inversion Experiments at 25° C. with 1 gramme-molecule of HCl.

Time in minutes.	Solution contains— 1 gramme-molecule of cane sugar, 1 gramme-molecule of alcohol + 818·8 grammes of water in 1 litre.		Solution contains— 1 gramme-molecule of cane sugar, 1 gramme-molecule of calcium chloride + 844·1 grammes of water in 1 litre.	
	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.	Rotation.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.
	° ′		° ′	
0	17 15	—	9 58	—
30	8 43	621	−1 27	1313
35	7 34	625	−2 35	1320
40	6 33	624	−3 32	1325
45	5 36	624	−4 19	1322
50	4 43	624	−4 58	1314
55	3 55	622	−5 31	1306
60	3 7	624	−6 4	1314
65	2 26	622	−6 30	1313
70	1 45	623	−6 52	1310
75	1 8	622	−7 11	1308
80	+0 33	623	−7 27	1304
85	+0 1	623	−7 43	1313
90	−0 27	620	−7 56	1317
95	−0 55	620	−8 5	1306
100	−1 22	621	−8 14	1304
	−7 13	—	−9 11	—
	Mean	623	Mean	1313

Table XII.

Conductivity of Chlorhydric Acid in presence of Galactose (volume-normal).

Galactose in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.					
	1. A.	2. A.	4. A.	8. A.	128. A.	128. B.
180	238·1	130·1	67·69	34·97	2·138	2·255
90	281·3	153·9	80·57	41·27	2·647	2·726
0	327·9	179·4	93·67	48·39	3·211	3·211

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No galactose.	1 gramme-molecule galactose per litre.			0·5 gramme-molecule galactose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327·9	238·1	237·6	0·5	281·3	281·5	− 0·2
2	358·8	260·2	260·0	0·2	307·8	308·1	− 0·3
4	374·7	270·8	271·5	− 0·7	322·3	321·7	0·6
8	387·1	379·8	280·5	− 0·7	330·2	332·4	− 2·2
*128 A	411·0	273·7	297·8	−24·1	338·8	352·9	−14·1
128 B	Puriss. galactose	288·6	297·8	− 9·2	348·9	352·9	− 4·0

$$C_m = C_0(1 - 0{\cdot}2902m + 0{\cdot}0148m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the galactose per litre.

Table XIII.

Conductivity of Chlorhydric Acid in presence of Mannitol (volume-normal).

Mannitol in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.				
	1.	2.	4.	8.	128.
182	235·9	129·3	67·43	34·71	2·234
91	281·0	153·9	80·32	41·30	2·693
0	327·9	179·4	93·67	48·39	3·211

* Impure material, *vide* p. 283.

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No mannitol.	1 gramme-molecule mannitol per litre.			0·5 gramme-molecule mannitol per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327·9	235·9	236·1	−0·2	281·0	281·1	−0·1
2	358·8	258·6	258·3	0·3	307·8	307·6	0·2
4	374·7	269·7	269·7	—	321·3	321·3	—
8	387·1	277·7	278·7	−1·0	330·4	331·9	−1·5
128	411·0	286·0	295·9	−9·9	344·7	352·4	−7·7

$$C_m = C_0(1 - 0{\cdot}2902m + 0{\cdot}0101m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the mannitol per litre.

Table XIV.

Conductivity of Chlorhydric Acid in presence of Lactose (volume-normal).

Lactose in grammes per litre.	Dilution of acid in litres per gramme-molecule of HCl.				
	1.	2.	4.	8.	128.
180	243·0	133·3	69·40	35·59	2·309
90	283·3	155·4	81·31	41·89	2·750
0	327·9	179·4	93·67	48·39	3·211

Molecular Conductivities of Chlorhydric Acid.

Dilution of HCl.	No lactose.	0·5 gramme-molecule lactose per litre.			0·25 gramme-molecule lactose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	327·9	243·0	243·0	—	283·3	283·9	−0·6
2	358·8	266·6	265·9	0·7	310·8	310·6	0·2
4	374·7	277·6	277·7	− 0·1	325·2	324·4	0·8
8	387·1	284·7	286·9	− 2·2	335·1	335·1	—
128	411·0	278·9	304·6	−25·7	352·0	355·8	−3·8

$$C_m = C_0(1 - 0{\cdot}5563m + 0{\cdot}0768m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of lactose per litre.

Table XV.

Conductivity of Sulphuric Acid in presence of Glucose (volume-normal).

Glucose in grammes per litre.	Dilution of acid in litres per gramme-molecule.				
	1.	2.	4.	8.	128.
180	276·5	150·8	78·03	40·72	3·467
90	330·5	180·7	93·33	48·90	4·234
0	385·5	211·2	109·3	57·56	5·021

Molecular Conductivities of Sulphuric Acid.

Dilution of H_2SO_4.	No glucose.	1 gramme-molecule glucose per litre.			0·5 gramme-molecule glucose per litre.		
	Obs.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.
1	385·5	276·5	275·7	0·8	330·5	329·8	0·7
2	422·4	301·6	302·1	− 0·5	361·4	361·4	—
4	437·2	312·1	312·6	− 0·5	373·3	374·1	−0·8
8	460·5	325·8	329·3	− 3·5	391·2	394·0	−2·8
128	642·7	443·8	460·9	−17·1	542·0	549·9	−7·9

$$C_m = C_0(1 - 0{\cdot}2927m + 0{\cdot}00776m^2),$$

where C_m is the conductivity in presence of m gramme-molecules of the glucose per litre.

A Numerical Examination of the Optical Properties of Thin Metallic Plates.

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The optical properties of thin metallic plates have been investigated by a number of physicists.* One of the earliest workers in this field was MacCullagh.† He predicted from theory and verified by experiment that if light incident on a gold leaf were plane polarised the transmitted beam would be elliptically polarised. With the improvement in experimental methods since MacCullagh's day, and the gradual removal of obscurities from the theory of metallic reflection and transmission, we now expect much more than a mere general agreement between theory and experiment. We look for an almost exact *numerical* coincidence.‡

The condition of the reflected or transmitted beam is precisely described by means of two quantities—the ellipticity and the difference of phase between the components of the light polarised perpendicular and parallel to the plane of incidence. The object of the present paper is to obtain convenient formulæ for these quantities and to compare them with the results of experiments, selecting the most careful and the most recent that are available. We shall admit into our theory no principle that has not found general acceptance,§ and shall thus be enabled to decide whether such principles are sufficient to colligate all the facts. If they fail in this, it will behove us to look for new principles, or, by a scrutiny of our so-called "facts," to indicate in what way experimental errors have brought about an apparent conflict between fact and theory.

Suppose that a ray of light is incident at an angle ϕ on a metal plate. If the plane of xy be taken as that of incidence, then an incident wave of

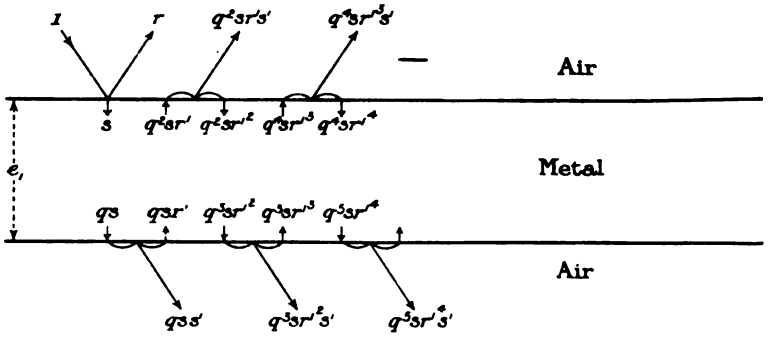
* See references in Mascart, 'Traité d'Optique,' vol. 2, p. 550, and Winkelmann, 'Handbuch der Physik,' vol. 6 (2), p. 1311. Neither of these, however, mentions the work of Conroy, 'Roy. Soc. Proc.,' vol. 31, 1881, p. 486.

† 'Roy. Irish Acad. Proc.,' vol. 1, p. 27, and 'Collected Works,' p. 82.

‡ See, *e.g.*, 'Roy. Soc. Proc.,' A, vol. 77, 1906, p. 211.

§ Of recent investigations the most elaborate is that of M. Meslin, 'Ann. de Chimie et de Phys.,' 1890, pp. 56—177. After giving the results of experiments, M. Meslin obtains, empirically, a formula for the difference of phase produced by transmission through a plate. He then makes an ingenious attempt to deduce this formula from theory. His argument, however, contains too many special hypotheses and assumptions to be final.

unit amplitude will be represented by a vector of the form $e^{ip[t-V^{-1}(x\cos\phi+y\sin\phi)]}$, where $p/2\pi$ is the frequency, t the time, V the velocity of light in air. This incident wave will give rise to a reflected wave represented by $re^{ip[t+V^{-1}(x\cos\phi-y\sin\phi)]}$ and a refracted wave $se^{ip[t-V^{-1}(bx+y\sin\phi)]}$. The dynamical equation requires that $b^2+\sin^2\phi=\mu^2$, where μ is a complex of the form $\mu_1-i\alpha$. Here μ_1 is the "refractive index" of the metal, *i.e.*, the ratio of the velocity of light in air to that in the metal, and α is the coefficient of absorption.



The refracted wave $se^{ip[t-V^{-1}(bx+y\sin\phi)]}$, which we shall refer to briefly as the wave s, will, after traversing the plate, become qs. When it reaches the bounding surface it will be reflected and refracted. In this way waves will surge to and fro across the plate, while an infinite series of waves will return into the first medium (air) and constitute the reflected beam, and another series will pass into the third medium (air) and constitute the transmitted beam.

We shall denote by r' and s' the quantities corresponding to r and s when we are considering a passage from metal to air instead of from air to metal. With this notation the reflected beam is represented by

$$r+q^2ss'r'+q^4ss'r'^2+\ldots=r+\frac{q^2ss'r'}{1-q^2r'^2},$$

and the transmitted beam by

$$qss'+q^3ss'r'^2+q^5ss'r'^4+\ldots=\frac{qss'}{1-q^2r'^2}.$$

The values of the quantities r and r', s and s' are given by the theory of reflection and refraction, and in this way we can easily prove that $r+r'=0$, and $ss'=1-r^2=1-r'^2$. These results can also be obtained by means of Stokes' principle of reversion, or by noting that when the thickness of the metal is indefinitely diminished and q becomes unity, then all the light is transmitted and none reflected.

Making use of these relations, the reflected beam becomes $r(1-q^2)/(1-q^2r^2)$

and the transmitted beam $q(1-r^2)/(1-q^2r^2)$. It thus appears that everything will be determined when q and r are obtained.

The first refracted wave was $se^{ip[t-V^{-1}(bx+y\sin\phi)]}$, where $b^2+\sin^2\phi=\mu^2$. Hence, if e_1 be the thickness of the plate, we have $q=e^{-ipbe_1V^{-1}}=e^{-i2\pi be_1\lambda^{-1}}$, where λ is the wave-length of the incident light. Putting $\mu=\mu_1-i\alpha=Me^{-i\alpha}$, we have $M^2=\mu_1^2+\alpha^2$, $\tan\alpha=\alpha/\mu_1$, $b=+(\mu^2-\sin^2\phi)^{\frac{1}{2}}=me^{-i\chi}$, where $m^4=M^4+\sin^4\phi-2M^2\cos 2\alpha\sin^2\phi$, and $\tan 2\chi=M^2\sin 2\alpha/(M^2\cos 2\alpha-\sin^2\phi)$. We thus get $q^2=Qe^{-i\psi}$, where $Q=e^{-4\pi e_1\lambda^{-1}m\sin\chi}$ and $\psi=4\pi e_1\lambda^{-1}m\cos\chi$. These relations suffice to determine Q in terms of the optical constants of the metal and the thickness of the plate. The quantity r is also a complex. Its value is given by the theory of reflection and proves to be dependent on the position of the plane of polarisation of the incident light. If we regard the transition from one medium to the other to be abrupt, then, when the incident light is polarised perpendicularly to the plane of incidence, r is given by Fresnel's formula

$$r_1=\frac{\mu\cos\phi-\cos\phi'}{\mu\cos\phi+\cos\phi'}=\frac{\tan(\phi-\phi')}{\tan(\phi+\phi')}.$$

For light polarised parallel to the plane of incidence, we have the corresponding formula

$$r_2=\frac{\cos\phi-\mu\cos\phi'}{\cos\phi+\mu\cos\phi'}=\frac{-\sin(\phi-\phi')}{\sin(\phi+\phi')}.$$

We have $\sin\phi=(\mu_1-i\alpha)\sin\phi'$,

and putting $\cos\phi'=ce^{-iu}=(1-M^{-2}\sin^2\phi e^{2i\alpha})^{\frac{1}{2}}$,

we get*

$$r_1=R_1e^{i\theta_1},\quad\text{where}\quad R_1^2=\frac{1-x_1}{1+x_1}\quad\text{and}\quad x_1=\frac{2Mc\cos\phi\cos(\alpha-u)}{M^2\cos^2\phi+c^2},$$

while $$\tan\theta_1=\frac{-2Mc\cos\phi\sin(\alpha-u)}{M^2\cos^2\phi-c^2}.$$

Similarly

$$r_2=R_2e^{i\theta_2},\qquad R_2^2=\frac{1-x^2}{1+x^2},\qquad x_2=\frac{2Mc\cos\phi\cos(\alpha+u)}{M^2c^2+\cos^2\phi},$$

$$\tan\theta_2=\frac{-2M\cos\phi\sin(\alpha+u)}{M^2c^2-\cos^2\phi}.$$

If the incident wave be represented by 1, then the reflected beam is similarly represented by $R'e^{i\theta'}$, where R' is the amplitude and θ' the change of phase produced by reflection. We have

$$R'e^{i\theta'}=\frac{r(1-q^2)}{1-q^2r^2}=\frac{Re^{i\theta}(1-Qe^{-i\psi})}{1-QR^2e^{i(2\theta-\psi)}}.$$

* 'Roy. Soc. Proc.,' A, vol. 77, 1906, p. 212.

We thus get

$$R'^2 = R^2 \frac{1+Q^2-2Q\cos\psi}{1+Q^2R^4-2QR^2\cos(2\theta-\psi)}$$

$$= R^2 \frac{1+Q^2-2Q\cos\psi}{1+Q^2R^4-2QR^2\cos(\psi+\gamma)},$$

where $2\theta = 360°-\gamma$.

This determines the intensity of the reflected beam. When the thickness of the plate is indefinitely small $Q = 1$ and $\psi = 0$. Hence $R'^2 = 0$, so that there is no reflected beam. As the thickness increases, Q approaches the limit zero, so that R'^2 approaches the limit R^2—as is to be expected. It may be interesting to observe, however, that the intensity of the reflected light may be greater for a thin plate than for a very thick one. We have $R' = R$ when

$$1+Q^2-2Q\cos\psi = 1+Q^2R^4-2QR^2\cos(\psi+\gamma),$$

$$\cos\psi - R^2\cos(\psi+\gamma) = \tfrac{1}{2}Q(1-R^4),$$

$$\sin(\psi-\gamma') = \frac{Q(1-R^4)}{2(1-2R^2\cos\gamma+R^4)^{\frac{1}{2}}},$$

where

$$\tan\gamma' = \frac{1-R^2\cos\gamma}{R^2\sin\gamma}.$$

Consider the case of direct incidence. We then have $\phi = 0$, $\psi = 4\pi e_1\lambda^{-1}\mu_1$, $Q = e^{-4\pi c_1\lambda^{-1}\alpha} = e^{-c_1\psi}$, where $c_1 = \tan\alpha$. The equation to determine ψ thus becomes

$$\sin(\psi+\gamma') = \frac{e^{-c_1\psi}(1-R^4)}{2(1-2R^2\cos\gamma+R^4)^{\frac{1}{2}}}.$$

For the silver and gold, to be considered later, c_1 is large, so that when ψ is not very small, the quantity $e^{-c_1\psi}$ will be very small, and we shall have $\sin(\psi+\gamma') = 0$ very approximately. This makes $\psi = \pi - \gamma'$. In the case of silver this makes $\frac{e^{-c_1\psi}(1-R^4)}{2(1-2R^2\cos\gamma+R^4)^{\frac{1}{2}}} = 8\times10^{-25}$. This is quite negligible, so that our approximation is sufficiently accurate for practical purposes.

Remembering that $e_1/\lambda = \psi/4\pi\mu_1$, we can thus easily find the thickness that gives $R' = R$. For the metals discussed later this gives $e_1/\lambda = 1{\cdot}136$ in the case of silver, and $e_1/\lambda = 0{\cdot}5343$ in the case of gold. If the thickness is rather greater than this, we have R′ greater than R, but as the thickness increases, R′ once more approaches to equality with R. There will then be some thickness that makes R′ a maximum, and it is not difficult to determine this thickness.

We have $\frac{R'^2}{R^2} = \frac{1+Q^2-2Q\cos\psi}{1+Q^2R^4-2QR^2\cos(\psi+\gamma)}$, and R'^2 is to be made a

maximum, it being observed that Q and ψ are functions of the thickness. Putting

$$\frac{e_1}{\lambda} = t_1; \quad Q = e^{-c_1\psi}; \quad \frac{dQ}{dt_1} = -c_1 Q \frac{d\psi}{dt_1}; \quad t_1 = \frac{\psi}{4\pi\mu_1};$$

we get, by equating dR'^2/dt_1 to zero,

$$[1+Q^2R^4-2QR^2\cos(\psi+\gamma)]\left[Q\frac{dQ}{dt_1}-\cos\psi\frac{dQ}{dt_1}+Q\sin\psi\frac{d\psi}{dt_1}\right]$$
$$=[1+Q^2-2Q\cos\psi]\left[R^4Q\frac{dQ}{dt_1}-R^2\cos(\psi+\gamma)\frac{dQ}{dt_1}+QR^2\sin(\psi+\gamma)\frac{d\psi}{dt_1}\right],$$

i.e. $[1+Q^2R^4-2QR^2\cos(\psi+\gamma)][-Q+\cos\psi+c_1^{-1}\sin\psi]$
$$=[1+Q^2-2Q\cos\psi][-R^4Q+R^2\cos(\psi+\gamma)+R^2c_1^{-1}\sin(\psi+\gamma)],$$

i.e., $[\sin(\psi+\alpha)-R^2\sin(\psi+\gamma+\alpha)]+Q[2R^2\sin\gamma\cos\alpha-(1-R^4)\sin\alpha]$
$$+Q^2R^2[R^2\sin(\psi-\alpha)-\sin(\psi+\gamma-\alpha)]=0.$$

As Q is small, this can easily be solved by approximations. The first approximation gives

$$\sin(\psi+\alpha)-R^2\sin(\psi+\gamma+\alpha)=0,$$

i.e., $\cos(\psi+\gamma'+\alpha)=0, \qquad \gamma=\frac{3}{2}\pi-\alpha-\gamma'.$

For silver, this makes $Q = e^{-c_1\psi} = 6{\cdot}6 \times 10^{-24}$, which is so small that the first approximation is sufficiently accurate. The thickness that gives the greatest intensity of reflected light is determined by $e_1/\lambda = 1{\cdot}157$ in the case of silver, and $e_1/\lambda = 0{\cdot}5586$ in the case of gold. In both cases, however, the maximum value of R'^2 is *very* slightly greater than R^2.

The following table shows how the intensity of the reflected light depends on the thickness of the plate in the case of gold and silver. The intensity, of course, depends on the values of the optical constants α and μ_1, and these in turn vary with the colour of the incident light. From Drude's experiments* with well cleaned silver in sodium light, he calculated that $\alpha = 3{\cdot}67$, and $\mu_1 = 0{\cdot}18$, and from similar experiments by Conroy,† with gold in red light, we find that $\alpha = 3{\cdot}204$, and $\mu_1 = 0{\cdot}365$‡.

* 'Wied. Ann.,' vol. 39, p. 481.

† 'Roy. Soc. Proc.,' 1881, p. 486.

‡ These constants are deduced from observations of the Principal Incidence and the Principal Azimuth. It has often been observed that these angles vary considerably with different conditions of the reflecting surface. That this is to be expected is apparent if we regard the transition from one medium to the other as gradual and not abrupt. The Principal Incidence and Principal Azimuth depend on the nature of the layer of transition, and when the matter is examined carefully it is found that the neglect of the transition layer may lead to considerable errors in the values of the optical constants. See 'Roy. Soc. Proc.,' 1906, p. 211, and *post*, p. 330, note †. For the present we shall take the value derived from the experiments of Drude and Conroy on the hypothesis of an abrupt transition as forming a sufficiently accurate first approximation to the truth.

e_1/λ.	Indef. small.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.	∞ .
Silver R'^2.....	0	0·0020	0·0610	0·1632	0·4301	0·8260	0·9383	0·9516	0·9517
Gold R'^2	0	0·0012	0·0289	0·1012	0·2922	0·6803	0·8504	0·8794	0·8796

These results are represented graphically in fig. 1 below.

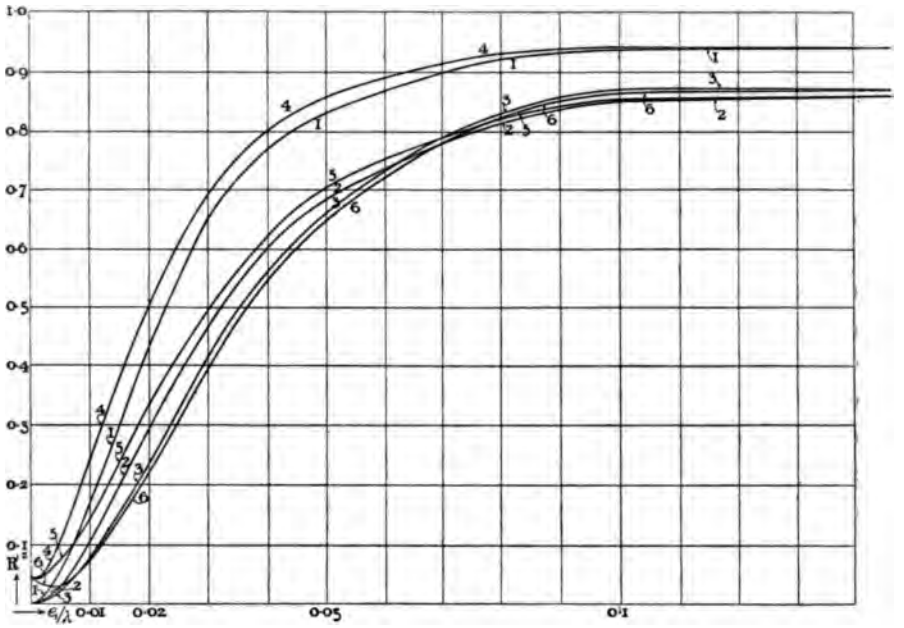


FIG. 1.

Curve 1 represents the silver and Curve 2 the gold. It will be seen that in both cases there is very little change in the intensity after a thickness of one-tenth of the wave-length has been reached. For that thickness the value of R'^2 is nearly 99 per cent. of that for a thick plate.

The formula for $R'e^{i\theta'}$ on p. 298 also enables us to calculate θ', the change of phase produced by reflection. We have $\theta' = \theta + \Phi' - \Phi$, where

$$\tan\Phi = \frac{-QR^2\sin(2\theta-\psi)}{1-QR^2\cos(2\theta-\psi)} = \frac{QR^2\sin(\psi+\gamma)}{1-QR^2\cos(\psi+\gamma)},$$

and Φ' is obtained from Φ by putting $R = 1$ and $\mu = 0$. As the thickness increases Q diminishes rapidly, so that Φ and Φ' approach the limit zero, and θ' approaches asymptotically the value θ, as is to be expected. In doing this, however, θ' may pass through a maximum and be greater than θ, so that the change of phase produced by a thin plate may be greater than that produced by a thick plate—as we have already seen is the case with the intensity.

We have $\theta' = \theta$ when $\Phi' = \Phi$, *i.e.*,

$$\frac{QR^2 \sin(\psi+\gamma)}{1-QR^2\cos(\psi+\gamma)} = \frac{Q\sin\psi}{1-Q\cos\psi},$$

$$\cos\psi\,[R^2\sin\gamma] - \sin\psi\,[1-R^2\cos\gamma] = QR^2\sin\gamma,$$

$$\cos(\psi+\gamma') = \frac{QR^2\sin\gamma}{(1-2R^2\cos\gamma+R^4)^{\frac{1}{2}}} = e^{-c_1\psi}\frac{R^2\sin\gamma}{(1-2R^2\cos\gamma+R^4)^{\frac{1}{2}}}.$$

This is satisfied, very approximately, by $\psi+\gamma' = \frac{1}{2}\pi$. For silver this corresponds to $e_1/\lambda = 0{\cdot}441$, and for gold $e_1/\lambda = 0{\cdot}192$.

To make θ' a maximum we must have

$$[\cos\psi - c_1\sin\psi - Q][1-2QR^2\cos(\psi+\gamma)+Q^2R^4]$$
$$= R^2[1-2Q\cos\psi+Q^2][\cos(\psi+\gamma)-c_1\sin(\psi+\gamma)-QR^2],$$

i.e., $[\cos(\psi+\alpha)-R^2\cos(\psi+\alpha+\gamma)]-Q[(1-R^4)\cos\alpha+2R^2\sin\gamma\sin\alpha]$
$$-2Q^2R^2\sin\tfrac{1}{2}\gamma\sin(\psi-\alpha+\tfrac{1}{2}V) = 0.$$

As a first approximation $\cos(\psi+\alpha) - R^2\cos(\psi+\alpha+\gamma) = 0$, *i.e.*, $\sin(\psi+\alpha-\gamma') = 0$, so that $\psi+\alpha+\gamma' = \pi$. For both silver and gold this will be found to make ψ nearly unity, so that Q is very small, and the first approximation is sufficiently close. The maximum value of θ' occurs when $\psi+\gamma' = \pi-\alpha$ and we have seen that $\theta' = \theta$ when $\psi+\gamma' = \frac{1}{2}\pi$. α is less than $\frac{1}{2}\pi$, so that $\pi-\alpha$ is greater than $\frac{1}{2}\pi$; but in the case of the silver and gold, already discussed, it is not very much greater, so that the maximum is reached soon after θ' is equal to θ. For silver the maximum occurs when $e_1/\lambda = 0{\cdot}455$ and for gold when $e_1/\lambda = 0{\cdot}216$.

The following table gives the value of θ', *expressed as a fraction of the half wave-length.*

e_1/λ.	Indef. small.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.	∞.
Silver θ'	0·5288	0·5417	0·5905	0·6410	0·7171	0·8061	0·8288	0·8312	0·8312
Gold θ'	0·5658	0 5771	0 6095	0·6473	0·7050	0·7832	0·8072	0·8095	0·8095

These results are represented graphically in fig. 2 below, Curve 1 corresponding to the silver and Curve 2 to the gold.

Perhaps the most striking thing about these results is the large percentage of the change of phase due to a thick plate which is produced by a very thin plate. In the one case 64 per cent. and in the other 70 per cent. of the total change is produced by an *indefinitely* thin plate. It must be borne in mind, however, that the intensity of the reflected light for such thicknesses is vanishingly small, so that it would not be practicable to measure the

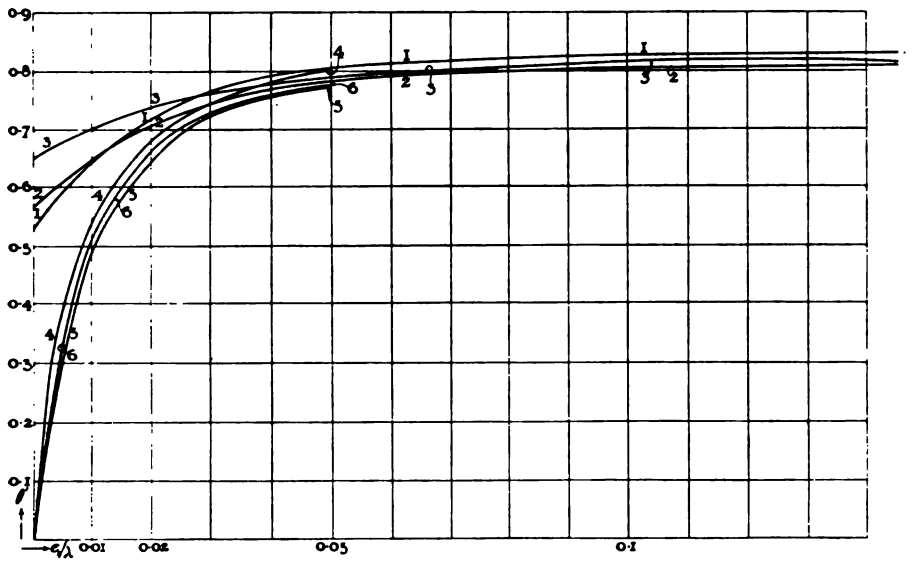


FIG. 2.

change of phase even if such thin plates were available. And in any case we should not be justified in pushing our analysis to the extreme of "vanishing" thinness, for when we approach molecular dimensions the fundamental hypothesis that the granular structure of reality can be replaced for optical purposes by a *continuum* ceases to be tenable.

Few accurate measurements seem to have been made on the intensity and change of phase in the case of reflection from a thin metal plate with air surrounding it. *Extreme* tenuity can be obtained only by depositing the metal chemically or electrically on some other material, such as glass. This, as we shall see later, completely alters the character of the reflected light when the thickness of the metal is small; but before this matter is discussed it will be convenient to investigate the nature of the transmitted beam for a metal plate surrounded by air.

For the transmitted beam we have

$$R'e^{i\theta} = \frac{q(1-r^2)}{1-q^2r^2},$$

so that the intensity is

$$R'^2 = \frac{Q(1+R^4-2R^2\cos 2\theta)}{1+Q^2R^2-2QR^2\cos(2\theta-\psi)} = \frac{Q(1+R^4-2R^2\cos\gamma)}{1+Q^2R^4-2QR^2\cos(\psi+\gamma)}.$$

As the thickness of the plate increases Q diminishes rapidly, so that the intensity of the transmitted light diminishes rapidly to zero. The following table gives the intensity for the gold and silver already discussed:—

e_1/λ.	Indef. small.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.	∞.
Silver R^2.....	1	0·9608	0·8705	0·7418	0·4644	0·1	0·0094	0·0001	0
Gold R^2	1	0·9605	0·9050	0·7820	0·5423	0·1541	0·0201	0·0007	0

These results are represented graphically in fig. 3.

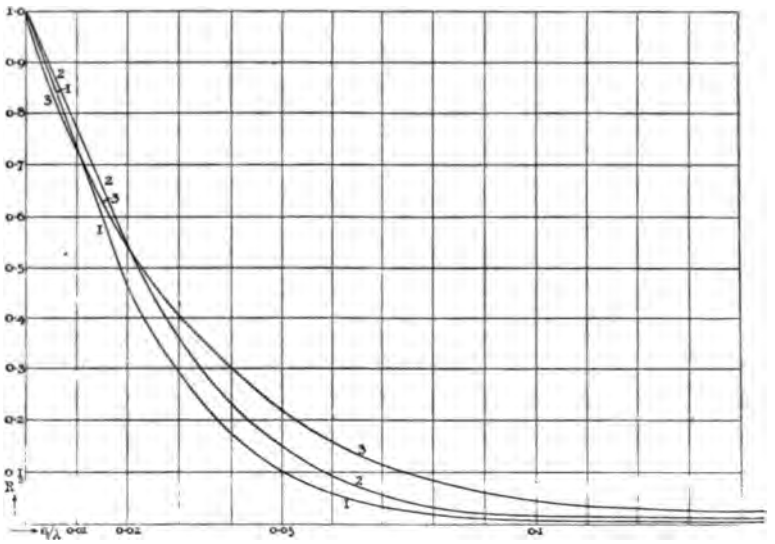


FIG. 3.

In this figure Curve 1 corresponds to the silver and Curve 2 to the gold. A silver plate whose thickness is one-tenth of the wave-length is practically opaque.

The change of phase is given by $\theta' = \Phi'' - \Phi - \frac{1}{2}\psi$, where Φ has the same value as on p. 301, and Φ'' is obtained from Φ by putting $Q=1$ and $\psi=0$. As the thickness increases Φ rapidly diminishes, so that the change of phase is soon represented by $\Phi'' = \frac{1}{2}\psi$. Φ'' is a constant, while $\frac{1}{2}\psi$ increases with the thickness, so that, after a certain thickness has been reached, θ' diminishes steadily and ultimately becomes negative. (It must be remembered that meanwhile Q diminishes rapidly and the intensity of the transmitted light becomes vanishingly small.) Φ diminishes at first more rapidly than $\frac{1}{2}\psi$ increases, so that θ' will begin by increasing and will afterwards diminish. It must, therefore, pass through a maximum and we proceed to determine the thickness of metal that will produce this maximum change of phase. Φ'' is a constant, so that we have to make $\Phi + \frac{1}{2}\psi$ a minimum. Remembering

that $\tan\Phi=\dfrac{QR^2\sin(\psi+\gamma)}{1-QR^2\cos(\psi+\gamma)}$ and that $Q=e^{-c_1\psi}$, we get, to determine the maximum of θ', the equation

$$1-2c_1QR^2\sin(\psi+\gamma)-Q^2R^4=0.$$

I.e.,

$$\sin(\psi+\gamma)=\frac{1}{2c_1}\left[\frac{e^{c_1\psi}}{R^2}-\frac{R^2}{e^{c_1\psi}}\right].$$

This is easily solved by successive approximations, and yields $c_1/\lambda=0{\cdot}078$ in the case of silver, and $c_1/\lambda=0{\cdot}068$ in the case of gold.

The value of θ', expressed as a fraction of the half wave-length, is given in the following table, and the results are represented graphically in fig. 4 below. As before, Curve 1 corresponds to the silver and Curve 2 to the gold.

c_1/λ.	Indef. small.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.
Silver θ'	0	0·0123	0·0642	0·1111	0·1872	0·2707	0·2787	0·2456
Gold θ'	0	0·0111	0·0432	0·0808	0·1374	0·2055	0·2018	0·1277

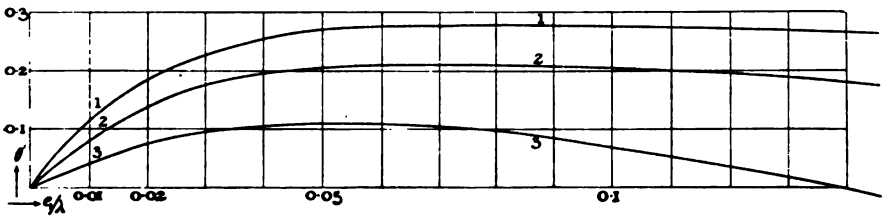
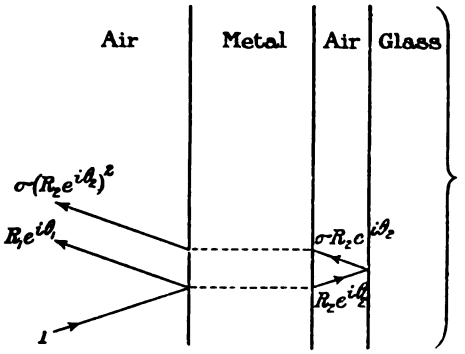


FIG. 4.

We shall now consider to what extent the results already obtained as to the intensity and change of phase of the reflected light are modified when the metal is deposited on glass. The second reflection and refraction in the investigation of p. 297 now takes place at a passage from metal to glass instead of at one from metal to air. The quantities r' and s' will therefore be altered, the new values being given, as before, by Fresnel's formulæ. This method of attacking the problem is adopted later (p. 313), when we are dealing with the more general case of incidence at any angle. As, however, we have already calculated the amplitude and phase of the reflected and transmitted beam for a metal plate surrounded by air, it is convenient to utilise these results in the present problem. To enable us to do this we can suppose the metal and glass separated by an *indefinitely thin* layer of air. An incident wave of unit amplitude gives rise to a reflected wave $R_1e^{i\theta_1}$,

where R′ and θ_1 are the R′ and θ' already calculated for the reflected wave. It also produces a transmitted wave $R_2 e^{i\theta_2}$ (R_2 and θ_2 having also been calculated). This wave is *immediately* reflected by the glass, giving a wave



$\sigma R_2 e^{i\theta_2}$. $\sigma R_2 e^{i\theta_2}$ in its turn is transmitted through the metal plate and emerges into the air as a wave $(\sigma R_2 e^{i\theta_2}) R_2 e^{i\theta_2} = A e^{i\chi}$ say. The complete reflected wave is thus the resultant of the two components $R_1 e^{i\theta_1}$ and $A e^{i\chi}$. If, as before, we denote it by $R' e^{\theta'}$, we have

$$R'^2 = R_1^2 + A^2 + 2R_1 A \cos(\theta_1 - \chi)$$

and

$$\tan \theta' = \frac{R_1 \sin \theta_1 + A \sin \chi}{R_1 \cos \theta_1 + A \cos \chi}.$$

If the incidence be direct, then σ is given by Fresnel's formula $\sigma = \frac{\mu-1}{\mu+1}$, where μ is the refractive index of the glass. Thus $A = \frac{\mu-1}{\mu+1} \cdot R_2^2$ and $\chi = 2\theta_2$.

For small thicknesses R_1 is very small, while R_2 is considerable. Under these circumstances R′ is nearly equal to A and θ' to χ. As the thickness increases, R_2 rapidly diminishes, so that R′ and θ' approximate more and more closely to R_1 and θ_1. Thus, except for very thin plates, the results will be the same as if the metal were surrounded by air instead of being deposited on glass. With very thin plates, however, the two cases will be quite different.

Taking $\mu = 1{\cdot}54$ we get the following values of R′².

e_1 λ.	Indef. small.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.	∞.
Silver R′²	0·0452	0·0419	0·1068	0·2411	0·5012	0·8525	0·9408	0·9516	0·9517
Gold R′²	0·0452	0·0405	0·0621	0·1336	0·3327	0·7025	0·8528	0·8794	0·8796

These results are represented graphically in fig. 1 above. Curve 4 corresponds to the silver and Curve 5 to the gold. A comparison of Curves 1 and 4 or Curves 2 and 5 will show the influence of the glass on the intensity of the reflected light.

The difference of phase (θ') is given in the following table.

e_1/λ.	Indef. small.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.	∞ .
Silver θ'	0	0·0946	0·3900	0·5356	0·6795	0·8005	0·8283	0·8312	0·8312
Gold θ'.....	0	0·0746	0·2886	0·4968	0·6427	0·7718	0·8056	0·8095	0·8095

Fig. 2 above gives a graphical representation of these results, Curve 4 for the silver and Curve 5 for the gold. As is to be expected, the difference between metal alone and metal on glass is very marked for small thicknesses. In all cases the change of phase is less for metal on glass than for metal alone, but the difference between the two cases diminishes rapidly as the thickness increases. After a thickness $e_1/\lambda = 0{\cdot}05$ has been reached there is scarcely any appreciable difference between the results, and for the sake of clearness the curves for metal on glass have not been drawn beyond this point.

If we compare these results with Wiener's observations* of the change of phase produced by reflection from thin films of silver deposited chemically on glass, we see that there is a close agreement. The change of phase takes place rapidly, not so rapidly as with Wiener's first mirror (A), but more rapidly than with his second mirror (B). With the silver, discussed above, about 65 per cent. of the total change of phase is reached when $e_1/\lambda = 0{\cdot}01$, *i.e.*, when $e_1 = 5{\cdot}89 \times 10^{-6}$ mm. $= 5{\cdot}89\,\mu\mu$. With Wiener's first mirror almost the whole change took place within a thickness $4\,\mu\mu$, but with the second mirror the corresponding thickness was $12\,\mu\mu$.

So far we have been occupied mainly with a discussion of the intensity and phase of the reflected and transmitted† light in the case of direct incidence. We shall now return to the more general problem stated at the onset, that of determining the ellipticity and the difference of phase between the parallel and perpendicularly polarised light for any angle of incidence. In the reflected light we have seen (p. 298) that $R'e^{i\theta'} = r(1-q^2)/(1-q^2r^2)$.

* 'Wied. Ann.,' vol. 31, p. 629.

† We have said nothing of the influence of the glass on the transmitted beam. It is shown later (p. 337) that for direct incidence the ellipticity is not affected by the glass.

Hence

$$\frac{R_1'}{R_2'}e^{i(\theta_1'-\theta_2')}=\frac{r_1(1-q^2r_2^2)}{r_2(1-q^2r_1^2)}=\frac{R_1}{R_2}e^{i(\theta_1-\theta_2)}\frac{1-QR_2^2e^{i(2\theta_2-\psi)}}{1-QR_1^2e^{i(2\theta_1-\psi)}}.$$

Thus if ϵ be the ellipticity and ω the azimuth of the reflected light we have

$$\tan^2\omega=\epsilon^2=\frac{R_1^2}{R_2^2}\frac{1+Q^2R_2^4-2QR_2^2\cos(\psi+\gamma_2)}{1+Q^2R_1^2-2QR_1^2\cos(\psi+\gamma_1)}.$$

As the thickness of the plate increases, Q diminishes and ϵ approaches the value R_1/R_2. We shall calculate ϵ for different thicknesses of the gold and silver already discussed.

If Δ be the difference of phase, we have $\Delta=\theta_2-\theta_1+\Phi_1-\Phi_2$, where Φ is given by the formula

$$\tan\Phi=\frac{QR^2\sin(\psi+\gamma)}{1-QR^2\cos(\psi+\gamma)}.$$

Having obtained Δ for a series of angles, we can represent the results graphically and so determine the angle of incidence that makes Δ equal to a quarter of the wave-length. This is the *Principal Incidence* and the corresponding value of ω is the *Principal Azimuth.*

We proceed to tabulate the values of the constants occurring in these formulæ for the silver whose optical constants are $\mu_1=0{\cdot}18$ and $\alpha=3{\cdot}67$. If $\mu=\mu_1-i\alpha=Me^{-i\alpha}$, we have $M^2=13{\cdot}5$ and $\alpha=87°\ 12'$. The other quantities are to be calculated from the formulæ

$$\sin\phi=\mu\sin\phi';\qquad\cos\phi'=ce^{-iu};\qquad\tan 2u=\frac{M^{-2}\sin^2\phi\ \sin 2\alpha}{1-M^{-2}\sin^2\phi\cos 2\alpha};$$

$$c^4=1-2M^{-2}\sin^2\phi\cos 2\alpha+M^{-4}\sin^4\phi;$$

$$m^4=M^4+\sin^4\phi-2M^2\cos 2\alpha\sin^2\phi;\qquad\tan 2\chi=\frac{M^2\sin 2\alpha}{M^2\cos 2\alpha-\sin^2\phi}.$$

The formulæ for Q, ψ, θ_1, θ_2, R_1, and R_2 have been already given on p. 298.

From these we get the following table. The values of log Q and ψ in this and later tables refer to the case $c_1/\lambda=0{\cdot}1$. As these quantities are directly

ϕ.	20°.	40°.	60°.	65°.	70°.	75°.	80°.	85°.
u	1′	6′	10′	11′	11′	12′	12′	12′
c	1·004	1·015	1·028	1·030	1·032	1·034	1·035	1·035
$\frac{1}{2}\gamma_1=180°-\theta_1$	32° 25′	39° 38′	58° 23′	67° 4′	78° 46′	94° 48′	116° 45′	145° 40′
$\frac{1}{2}\gamma_2=180°-\theta_2$	28° 33′	23° 12′	15° 5′	12° 44′	10° 18′	7° 47′	5° 14′	2° 37′
R_1^2	0·9491	0·9378	0·9156	0·9084	0·9028	0·9010	0·9105	0·9423
R_2^2	0·9548	0·9636	0·9766	0·9802	0·9842	0·9879	0·9919	0·9961
χ	87° 14′	87° 16′	87° 21′	87° 21′	87° 22′	87° 23′	87° 24′	87° 24′
m	3·691	3·730	3·775	3·784	3·792	3·798	3·804	3·806
ψ	12° 50′	12° 50′	12° 32′	12° 32′	12° 32′	12° 30′	12° 30′	12° 30′
log Q	3·989	3·967	3·942	3·936	3·933	3·929	3·926	3·925

proportional to the thicknesses, their values in other cases can be readily obtained by simple division or multiplication.

From these numbers and the formulæ above we derive the following table, giving the value of Δ expressed as a fraction of the half wave-length :—

e_1/λ.	$\phi = 20°$.	40°.	60°.	70°.	75°.	80°.	85°.
0·001	0·0404	0·1723	0·4524	0·7039	0·8966	1·132	1·404
0·005	0·0334	0·1428	0·3723	0·5821	0·7333	0·9245	1·148
0·01	0·0269	0·1150	0·3056	0·4922	0·6333	0·8222	1·045
0·02	0·0207	0·0900	0·2531	0·4269	0·5588	0·7365	0·938
0·05	0·0204	0·0874	0·2373	0·3878	0·4958	0·6506	0·8330
0·1	0·0214	0·0909	0·2404	0·3814	0·4848	0·6227	0·7977
0·2	0·0214	0·0913	0·2405	0·3804	0·4834	0·6193	0·7943

These results are exhibited graphically in figs. 5 and 6 below.

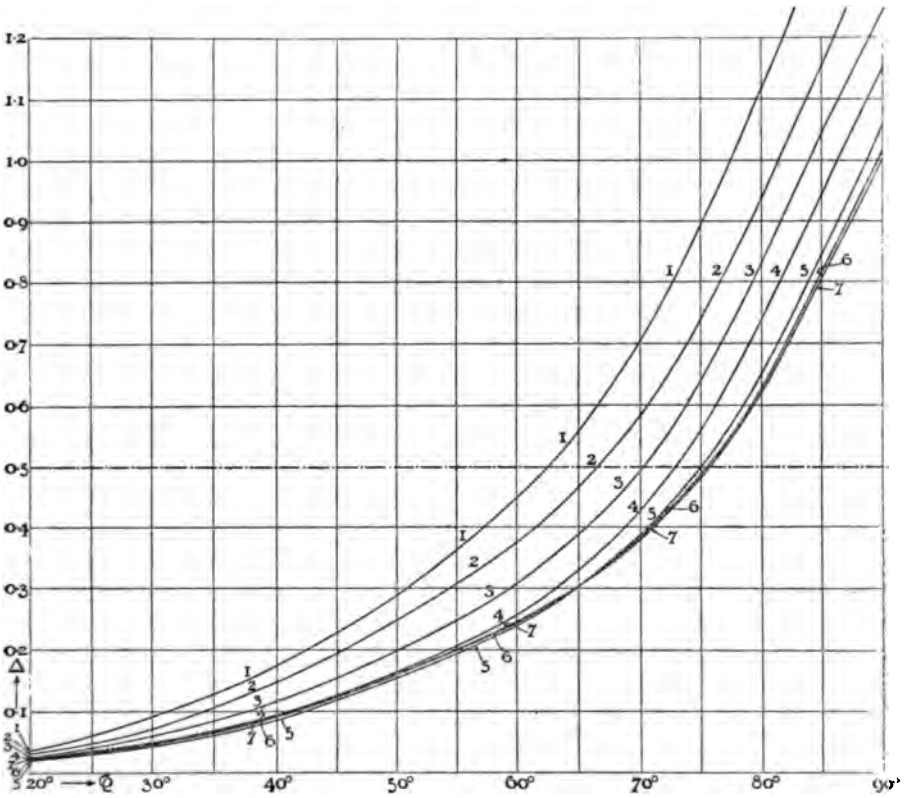


FIG. 5.

Fig. 5 represents Δ as a function of ϕ, the angle of incidence. The urves numbered 1 to 7 correspond to the seven different values of e_1/λ

in the above table, from 0·001 to 0·2. It will be seen that in all cases the difference of phase increases with the angle of incidence. From the graph we see that the values of the Principal Incidence for the various thicknesses dealt with are 62° 40′, 66° 30′, 70° 15′, 73°, 74° 30′, 75° 30′, 75° 48′. The Principal Incidence increases with the thickness, rapidly at first, but afterwards more slowly as it tends to the constant value appropriate to a thick plate. There is little further change in the value of the Principal Incidence when the thickness of the metal exceeds 0·00003 mm.

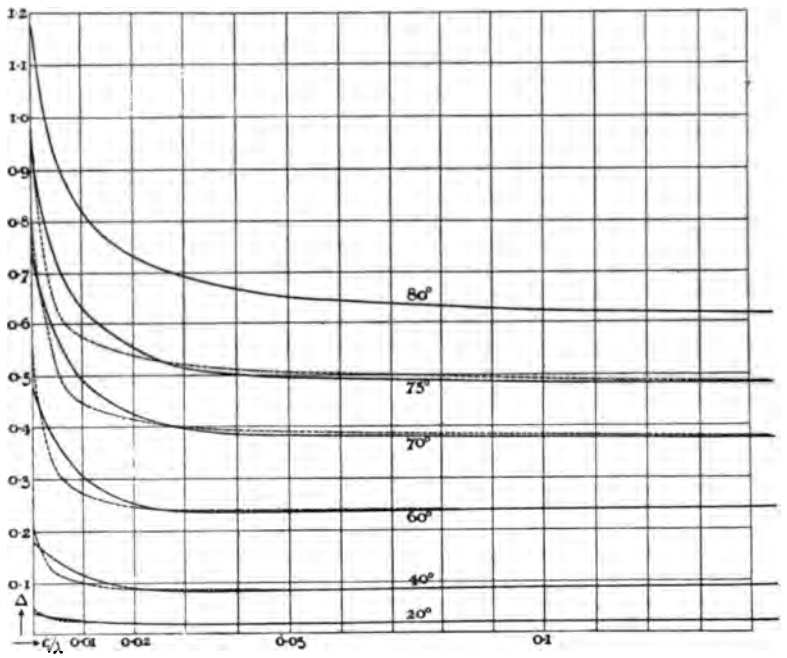


Fig. 6.

The continuous curves in fig. 6 above represent Δ as a function of the thickness for different angles of incidence. (The dotted curves refer to the case of silver films on glass, to be dealt with later.) These curves show how rapidly Δ diminishes as the thickness increases at first. For incidences of 60° and under, Δ begins by diminishing, and then very slowly increases again. The minimum value of Δ occurs when e_1/λ is in the neighbourhood of 0·05. For incidences of 70° and upwards there is no such minimum, and Δ continually diminishes until it reaches the value appropriate to a thick plate.

The azimuth (ω) is given in the following table :—

e_1/λ.	$\phi = 20°$.	40°.	60°.	70°.	75°.	80°.	85°.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′
0·001	41 42	31 47	17 9	10 29	7 58	6 7	7 38
0·005	41 57	32 35	18 48	12 40	10 36	9 49	12 50
0·01	42 22	34 19	22 15	16 57	15 28	15 52	22 0
0·02	43 18	38 0	29 35	25 41	24 48	26 16	33 30
0·05	44 39	43 7	40 34	39 8	39 0	39 57	42 37
0·1	44 53	44 29	43 46	43 21	43 15	43 28	44 7
0·2	44 55	44 37	44 5	43 46	43 41	43 46	44 12

These results are represented in figs. 7 and 8 below.

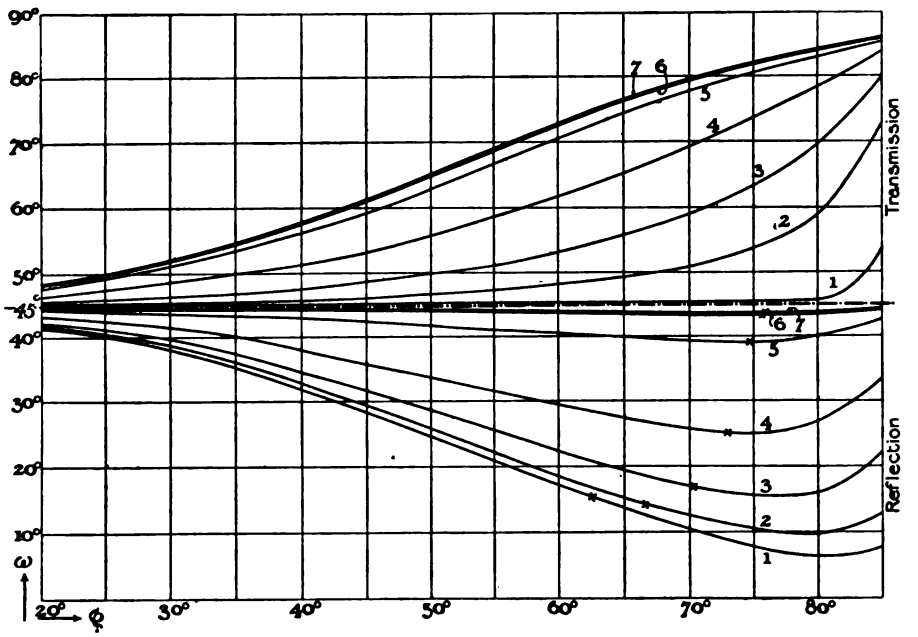


FIG. 7.

It will be seen that the azimuth is always less than 45°, so that for reflection R_1' is always less than R_2'. The case of reflection is represented by the part of the figure below the line $\omega = 45°$. Fig. 7 depicts ω as a function of the incidence for different thicknesses. It shows that the azimuth diminishes as the incidence increases, reaches a minimum, and then increases. The incidence at which ω is a minimum decreases as the thickness of the metal increases. From the figure we easily obtain the values of the Principal Azimuth for the different thicknesses, using the results already obtained for the Principal Incidence. The Principal Azimuth proves to be

15° 20′, 14°, 16° 45′, 24° 50′, 39° 10′, 43° 20′, and 43° 50′ in the different cases. It thus diminishes at first as the thickness increases, then increases rapidly until a thickness of 1/10 of the wave-length is reached, after which there is very little increase as the plate thickens. The values of the Principal Incidences and Principal Azimuths are indicated by the positions of the crosses (×) in the above figure.

Fig. 8 below represents the same quantity ω as a function of the thickness of the plate for different incidences. It shows how the azimuth increases with the thickness for values of e_1 less than 1/10 of the wave-length, and that beyond this there is very little change in ω.

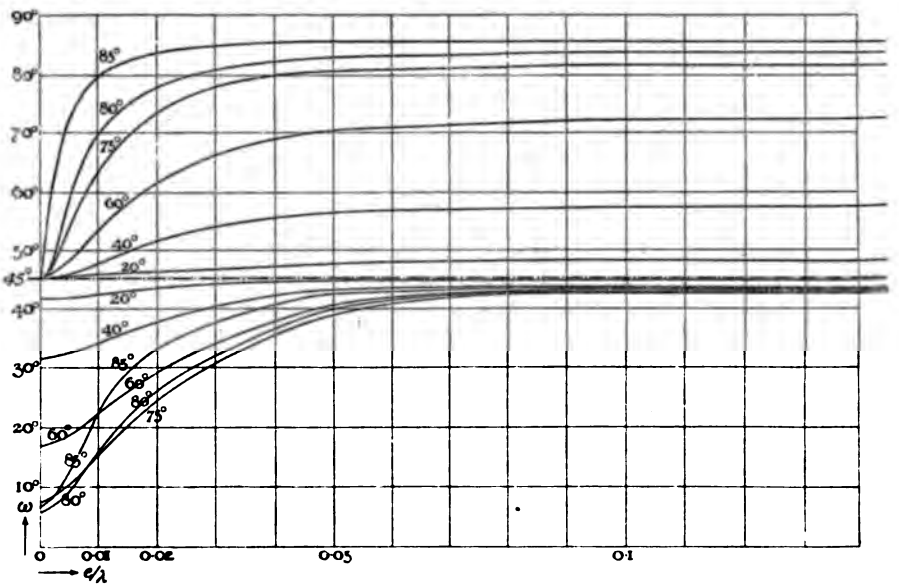
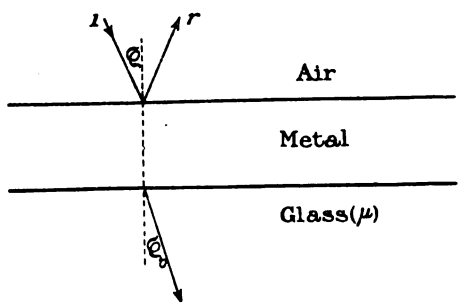


FIG. 8.

Before attempting to compare these results with experiment, we must see to what extent they are modified when the silver is deposited on glass, for it is under such conditions that most of the careful observations have been made.



In this case the reflected wave, instead of being $r(1-q^2)/(1-q^2r^2)$, is now $(r-q^2\rho)/(1-q^2r\rho)$, where r is the same as before, and ρ the corresponding quantity, when a ray of light goes from glass to metal instead of from air to metal. The quantity q is the same as before, and in calculating ρ we must replace M by M/μ and ϕ by ϕ_0, where $\sin\phi = \mu \sin\phi_0$ and μ is the coefficient of refraction of the glass. Putting $\rho = Pe^{i\omega}$ and taking $\mu = 1{\cdot}54$, we get the following set of values:—

ϕ.	20°.	40°.	60°.	65°.	70°.	75°.
$180°-\omega_1$	48° 13′	58° 3′	81° 27′	91° 13′	103° 19′	118° 20′
$180°-\omega_2$	42° 48′	35° 5′	23° 2′	19° 30′	15° 49′	11° 58′
P_1^2	0·9290	0·9177	0·9028	0·9010	0·9033	0·9118
P_2^2	0·9363	0·9475	0·9649	0·9705	0·9750	0·9838

We have $$\frac{R_1'}{R_2'}e^{i(\theta_1'-\theta_2')} = \frac{r_1-q^2\rho_1}{r_2-q^2\rho_2}\cdot\frac{1-q^2r_2\rho_2}{1-q^2r_1\rho_1}.$$

Thus the ellipticity (ϵ) is given by the formula

$$\epsilon^2 = \frac{R_1^2+Q^2P_1^2-2QR_1P_1\cos(\omega_1-\theta_1-\psi)}{R_2^2+Q^2P_2^2-2QR_2P_2\cos(\omega_2-\theta_2-\psi)} \times \frac{1+Q^2R_2^2P_2^2-2QR_2P_2\cos(\theta_2+\omega_2-\psi)}{1+Q^2R_1^2P_1^2-2QR_1P_1\cos(\theta_1+\omega_1-\psi)},$$

and the difference of phase (Δ) is

$$\chi_2-\chi_1+\Phi_1-\Phi_2,$$

where

$$\tan\chi = \frac{R\sin\theta-QP\sin(\omega-\psi)}{R\cos\theta-QP\cos(\omega-\psi)} \quad \text{and} \quad \tan\Phi = \frac{-QRP\sin(\theta+\omega-\psi)}{1-QRP\cos(\theta+\omega-\psi)}.$$

From these formulæ and the constants above we derive the following table for Δ.

e_1/λ.	ϕ = 20°.	40°.	60°.	65°.	70°.	75°.
0·001	0·0435	0·1833	0·4657	0·5732	0·6988	0·8567
0·005	0·0297	0·1186	0·3131	0·3967	0·4957	0·6294
0·01	0·0254	0·1014	0·2733	0·3479	0·4446	0·5744
0·02	0·0207	0·0901	0·2491	0·3204	0·4156	0·5419
0·05	0·0200	0·0884	0·2401	0·3057	0·3922	0·5086
0·1	0·0213	0·0911	0·2404	0·3024	0·3819	0·4856
0·2	0·0214	0·0913	0·2405	0·3018	0·3804	0·4834

These results are represented in fig. 6 above and fig. 9 below. The dotted curves in fig. 6 exhibit Δ as a function of the thickness of the film for different angles of incidence. The continuous curves of that figure

represent the corresponding values of Δ when there is no glass, so that a comparison of the two curves shows at once the modifications introduced by depositing the metal on glass. Quincke concluded from his experiments* that the difference of phase is always less for silver alone than for the same thickness of silver on glass. This agrees with our results for thicknesses greater than that given by $e_1/\lambda = 0{\cdot}03$, and it was on films of such thickness that Quincke experimented. The excess of Δ for silver on glass over its value for silver alone increases with the angle of incidence, but is always small. We see, moreover, that Quincke's conclusion is not applicable to films whose thickness is less than $0{\cdot}02\,\lambda$, except for *excessively* thin films.

Fig. 9 represents Δ as a function of ϕ for different thicknesses. The curve marked 0 corresponds to an *indefinitely* thin film of silver on the glass, the

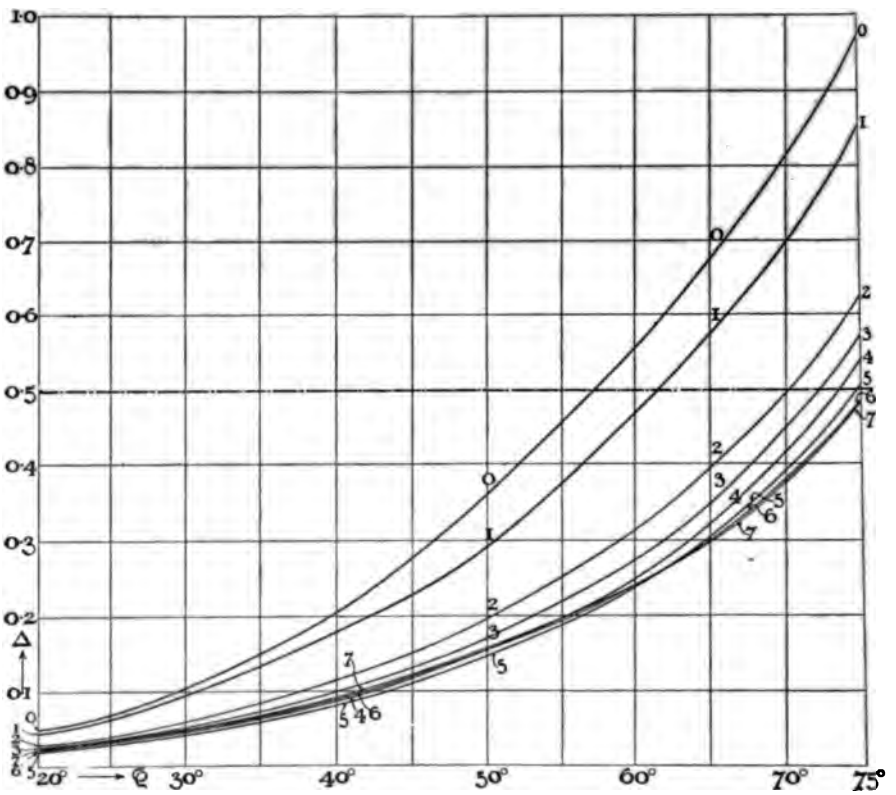


Fig. 9.

other curves to the different thicknesses mentioned in the table above. From the graph we obtain the following values of the Principal Incidences:— 57°, 61° 35′, 70° 12′, 72°, 73° 25′, 74° 45′, 75° 40′, 75° 48′. The angle 57° is

* 'Pogg. Ann.,' vol. 119, p. 368.

polarising angle of the glass, and we thus see that we can pass from 'eous reflection to metallic reflection through all the intermediate states the aid of layers of silver gradually increasing in thickness. One of most striking facts about these results is the very rapid change in the ıcipal Incidence produced by a slight thickening of the silver film when film is very thin. A film of only one-thousandth of the wave-length 'eases the Principal Incidence from 57° to 61° 35′. This indicates how ıiderable would be the influence of a surface layer of any kind on the tion of the Principal Incidence and serves to explain the observation of careful experimenters that the Principal Incidence alters with different litions of the reflecting surface.* It is also in good agreement with an ɛriment by Mascart† on the subject. A silver film was deposited on s by electrolysis. The film was so thin that its existence could not have ı suspected without previous knowledge. It was quite impossible to nate the thickness exactly, but it was certainly not greater than five- ısandths of a wave-length. Even with this thin film the properties of the t reflected from the glass were considerably modified and the Principal dence had increased from 57° to 59° 45′. Conroy made various experi- ts‡ with silver films on glass. The films varied in thickness from 5×10^{-6} cm. to $8{\cdot}995 \times 10^{-6}$ cm. Taking $\lambda = 5{\cdot}89 \times 10^{-5}$ cm. for ɔw light, this makes e_1/λ vary from 0·069 to 0·153. This range lies ween Curves 5 and 7 of the figure above. Our graph makes the Principal dence increase in this range from 74° 45′ to 75° 48°, an increase of 1° 3′. :oy found an increase of 2° 4′. Although the Principal Incidence changes lly at first, it soon tends to a constant value and there is little further ge when the thickness exceeds 0·00003 mm. Quincke§ made a large ber of observations with silver films and red light. He found that the es of the Principal Incidence increased with the thickness, tended to ɔnstant value and changed very little when the thickness of the silver exceeded 0·00002 mm. To exhibit more clearly the influence of the ; on the Principal Incidence the results for silver alone and for silver on ı are set out together and their differences stated.

* *Cf.* 'Roy. Soc. Proc.,' 1906, p. 211.
† 'Comptes Rendus,' vol. 76, p. 866.
‡ 'Roy. Soc. Proc.,' 1881, p. 486.
§ 'Pogg. Ann.,' vol. 129, p. 177.

e_1/λ.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′
P.I. (silver alone)	62 40	66 30	70 15	73 0	74 30	75 30	75 48
P.I. (silver on glass)	61 35	70 12	72 0	73 25	74 45	75 40	75 48
Difference	−1 5	+3 42	+1 45	+0 25	+0 15	+0 10	0

It appears from this that, except for excessively thin films, the Principal Incidence is greater for silver on glass than for the same thickness of silver alone. The difference, however, is nowhere very considerable, and it diminishes to zero as the thickness of the metal increases.

The ellipticity (ϵ) is given by the formula on p. 313; it is most conveniently expressed as the tangent of the azimuth, whose value is set out in the following table:—

e_1/λ.	$\phi = 20°$.	40°.	60°.	65°.	70°.	75°.
	°	° ′	° ′	° ′	° ′	° ′
0·001	44 47	44 25	43 20	42 37	41 29	40 13
0·005	43 42	39 51	32 6	29 5	26 3	22 46
0·01	43 28	37 37	28 22	25 50	22 40	19 54
0·02	43 21	38 38	31 19	29 34	28 15	26 41
0·05	44 29	42 59	40 28	40 1	40 9	41 22
0·1	44 51	44 27	43 44	43 22	43 23	43 24
0·2	44 54	44 36	44 5	43 23	43 46	43 41

Fig. 10 below exhibits these results graphically.

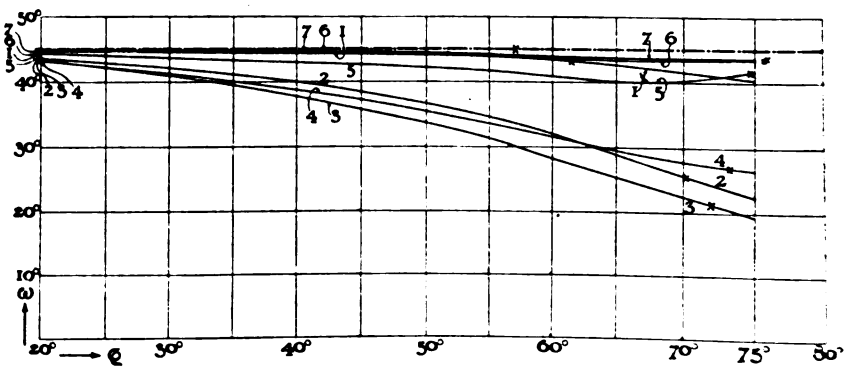


Fig. 10.

A comparison of figs. 7 and 10 will indicate clearly the change in the azimuth produced by depositing the silver on glass. It will be seen that Curves 4, 5, 6, and 7 in the two figures are very similar, so that after a thick-

ness 0·02 λ has been reached it does not make a great difference whether the silver is alone or resting on glass. As is to be expected, however, with very thin films the difference between the two cases is marked. On comparing Curves 1, 2, and 3 in the two figures we see that they are completely different. For silver alone the azimuth *increases* with the thickness, whereas for silver films on glass it *diminishes* rapidly at first. The Principal Incidence having been obtained above it is easy to determine the corresponding Principal Azimuth from the figure. The position of the Principal Incidence and Azimuth is marked in fig. 10 by a cross (×). The following table gives the Principal Azimuth for different thicknesses and compares it with the case of silver alone:—

e_1/λ.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′
P.A. (silver alone).....	15 20	14 0	16 45	24 50	39 10	43 20	43 50
P.A. (silver on glass)	43 15	25 40	21 20	27 10	41 15	43 30	43 50
Difference	27 55	11 40	4 35	2 20	2 5	0 10	0

The Principal Azimuth is thus always greater for silver on glass than for silver alone. The difference is very considerable for small thicknesses, but diminishes rapidly to zero as the thickness increases. When the thickness changes from 0·05 λ to 0·2 λ the Principal Azimuth increases 2° 25′. Conroy* found a much larger increase, viz., 14°, in the same range. It appears, however, that the variation of the Principal Azimuth with the thickness is very considerable in the neighbourhood of $e_1/\lambda = 0{\cdot}05$. When the thickness increases from 0·02 λ to 0·05 λ there is a change of 14° 5′ in the Principal Azimuth. Thus a slight error in the estimate of the thickness of the thinnest of Conroy's films would account for the apparent discrepancy between theory and experiment.†

Having discussed the nature of the light reflected from silver films, we proceed to estimate the extent to which these results are modified when films of some other metal are employed. So far our results have been obtained on the supposition that the transition from air to the metal is abrupt and not gradual. This, of course, is only an approximation to the truth; but in the case of silver the approximation has proved to be sufficiently close for colligating the experimental results. When the influence of the layer of

* Conroy, *loc. cit.*, p. 315.

† The thickness was calculated from the weight of a measured area. There was necessarily some uncertainty as to the density of the silver in so finely divided a state.

transition is considered it is found* that the difference of phase is altered by a quantity χ which is a maximum near the Principal Incidence, where it is given by the formula

$$\tan \chi = \frac{\sin^4 \phi - M^2 c^2 \cos^2 \phi}{2Mc \cos \phi \sin^2 \phi \sin (\alpha + u)}.$$

This enables us to determine for what metals the correction due to the layer of transition is most considerable; *e.g.*, it would lead us to expect that the influence of the layer would be greater with gold than with silver. As, however, the analysis is necessarily much more complex when there is a surface layer to be taken into account, we shall hold fast to the hypothesis of a sudden transition from one medium to the other as a sufficiently close approximation to the truth, unless we are driven from it by too great a discrepancy between theory and observation.

The metal that lends itself most readily to accurate experiments with thin plates is gold. Working with red light, Conroy found a Principal Incidence of 74° and a Principal Azimuth of 42° as the mean of several determinations. On the supposition of a sudden transition from air to gold the optical constants can be derived from these angles by means of the formulæ†

$$Mc = \frac{\sin^2 \phi}{\cos^2 \phi}, \qquad \omega = \frac{\alpha + u}{2},$$

coupled with the formulæ for c and u already given (p. 308). In this way we obtain $M^2 = 10{\cdot}4$ and $\alpha = 83° 30'$. With these constants and the formulæ on p. 308 we get the following table:—

ϕ.	30°.	40°.	50°.	60°.	70°.	80°.	85°.
u	9′	15′	21′	26′	30′	33′	34′
c	1·012	1·020	1·027	1·035	1·041	1·045	1·046
$180 - \theta_1$	27° 36′	31° 55′	39° 26′	53° 47′	84° 38′	136° 41′	160° 2′
$180 - \theta_2$	19° 43′	17° 12′	14° 12′	10° 53′	7° 22′	3° 43′	1° 52′
R_1^2	0·9105	0·9007	0·8867	0·8708	0·8570	0·8782	0·9251
R_2^2	0·9311	0·9414	0·9510	0·9614	0·9743	0·9865	0·9940
γ	83° 39′	83° 45′	83° 51′	83° 56′	84°	84° 3′	84° 4′
ω	3·264	3·288	3·312	3·336	3·357	3·369	3·372
ψ	26°	25° 46′	25° 34′	25° 24′	25° 15′	25° 8′	25° 4′
log Q	2·230	2·217	2·203	2·190	2·178	2·172	2·170

With the aid of these quantities we derive the following series of values of Δ from the formulæ of p. 308:—

* See 'Roy. Soc. Proc.,' 1906, p. 224.

† *Loc. cit.*, p. 213.

e_1/λ.	$\phi = 30°$.	40°.	50°.	60°.	70°.	80°.
0·001	0·0790	0·1490	0·2550	0·4323	0·7793	1·323
0·005	0·0605	0·1147	0·1977	0·3413	0·6422	1·110
0·01	0·0457	0·0852	0·1548	0·2797	0·5577	1·009
0·02	0·0363	0·0698	0·1261	0·2372	0·4945	0·9093
0·05	0·0403	0·0758	0·1324	0·2333	0·4498	0·7854
0·1	0·0435	0·0777	0·1398	0·2389	0·4331	0·7444
0·2	0·0439	0·0818	0·1403	0·2391	0·4292	0·7389

These results are represented in fig. 11 below.

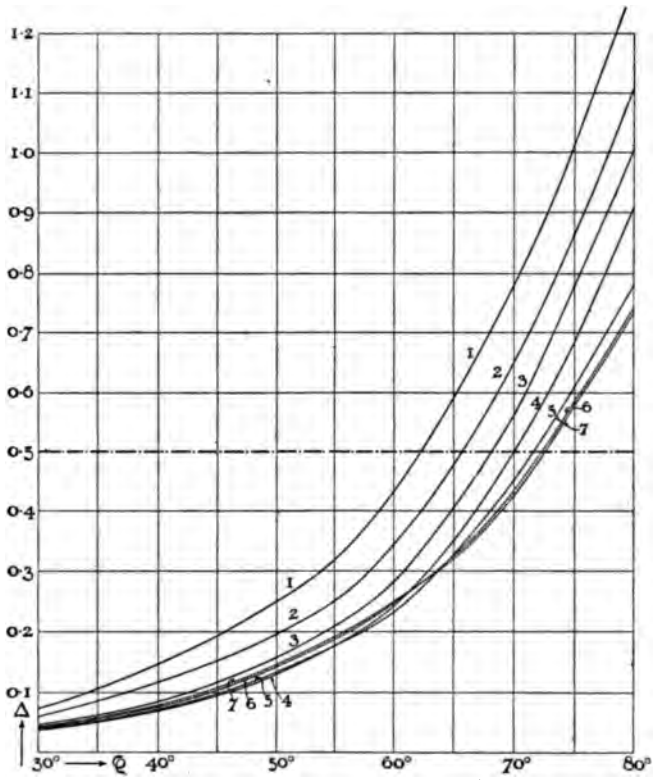


FIG. 11.

A comparison with fig. 5 will show that there is not much difference between the two metals as far as the difference of phase produced by reflection is concerned. Δ follows very much the same law in the two cases, as regards its dependence both on the angle of incidence and the thickness of the plate. The Principal Incidences corresponding to the various thicknesses are 62° 24′, 65° 40′, 68° 12′, 70°, 71° 45′, 72° 20′, and 72° 45′. The main difference is that the Principal Incidence is rather slower to reach its final

value for gold than for silver. For silver we found that when $e_1/\lambda=0{\cdot}2$ the Principal Incidence was the same as for a thick plate; for gold, however, when $e_1/\lambda=0{\cdot}2$ the Principal Incidence is still 1° 15′ from its final value.* Conroy experimented with gold leaves varying in thickness from $6{\cdot}45\times10^{-5}$ cm. to $1{\cdot}135\times10^{-5}$ cm. For red light, taking $\lambda=7{\cdot}6\times10^{-5}$ cm. this makes e_1/λ vary from 0·085 to 0·149. This range lies between the Curves 5 and 7 of fig. 11, and we see that the variation of the Principal Incidence is small. The increase is only about a degree, whereas Conroy found an increase of 1° 47′. The agreement is quite as close as could be expected considering the discrepancies between the different experimental results, the uncertainty as to the optical constants and the specific gravity† of the metal in the state of gold leaf, and the fact that we have neglected the influence of the glass on which the leaves were placed.‡ Conroy's conclusion that the Principal Incidence always increases with the thickness of the metal is supported by our theory with the optical constants that we have adopted for silver and gold. However, Meslin's experiments with gold over a much wider range of thickness show that the law is not universally applicable, and we shall see later that this is supported by theory when the transition layer is taken into consideration.

The azimuth (ω) is given in the following table:—

e_1/λ.	ϕ = 30°.		40°.		50°.		60°.		70°.		80°.		85°.	
	°	′	°	′	°	′	°	′	°	′	°	′	°	′
0·001	36	12	29	26	21	24	13	29	7	26	6	0	6	59
0·005	37	3	30	49	23	21	15	48	10	13	10	57	17	55
0·01	38	24	33	9	26	42	19	48	14	34	18	0	28	32
0·02	40	49	37	23	33	2	29	0	23	2	28	48	38	14
0·05	43	44	42	38	41	8	39	5	37	15	39	5	43	25
0·1	44	33	44	10	43	38	43	3	41	40	42	40	43	58
0·2	44	41	44	22	44	0	43	35	42	10	43	0	43	58

These results are exhibited in fig. 12 below.

On comparing this with fig. 7 above it will be seen that there is not much difference between the behaviour of the two metals. The Principal Azimuths for the various thicknesses are found from the figure to be 11° 45′, 12°, 15° 27°, 37° 20′, 41° 40′, and 42° respectively. The crosses (×) in the figure represent the positions of the Principal Incidence and Azimuth. From the

* It must be remembered that λ is not the same in the two cases, the incident light being yellow for silver and red for gold.

† This, of course, affects the estimate of the thickness, and a slight change in this would easily account for the apparent difference between theory and experiment.

‡ *Cf.* p. 316. For such thicknesses the effect of the glass is small.

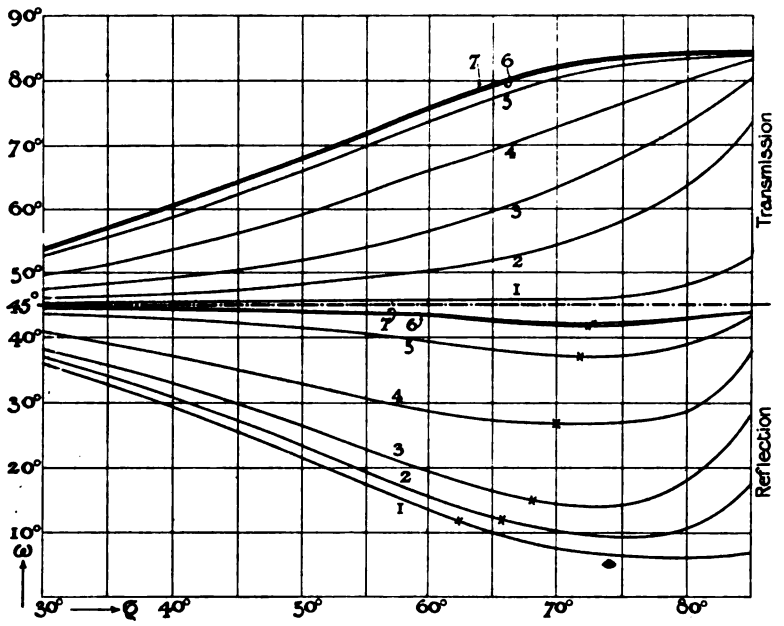


FIG. 12.

results of our investigation in the case of silver we should expect these angles to be very considerably altered if the gold were deposited on glass. The difference, however, would not be great for the thicknesses greater than 0·05 λ. It was with such thicknesses that the experiments of Conroy, referred to above, were carried out. Between the Curves 5 and 7 of the above figure the Principal Azimuth increases 2° 40′. Within the same range Conroy found an increase of about 2°. Conroy concluded that the Principal Azimuth always increases with the thickness. Our theory leads to a similar conclusion for a thin plate of gold surrounded by air, but if the gold were placed on glass the law of variation of the Principal Azimuth would be completely changed, as was found in the case of silver. The theory, however, is in satisfactory agreement with Conroy for thicknesses such as he employed in his experiments.

Transmission.

We shall now turn from the reflected light to consider in a similar manner the nature of the transmitted beam. We have seen (p. 298) that the transmitted beam is represented by $q(1-r^2)/(1-q^2r^2)$. Thus, with the same notation as in the case of reflection, we have

$$\frac{R_1'}{R_2'}e^{i(\theta_1'-\theta_2')} = \frac{1-r_1^2}{1-r_2^2}\frac{1-q^2r_2^2}{1-q^2r_1^2}.$$

Proceeding as on pp. 307 and 308, we get

$$\tan^2\omega = \epsilon^2 = \frac{1+R_1^4-2R_1^2\cos\gamma_1}{1+R_2^4-2R_2^2\cos\gamma_2}\cdot\frac{1+Q^2R_2^4-2QR_2^2\cos(\psi+\gamma_2)}{1+Q^2R_1^2-2QR_1^2\cos(\psi+\gamma_1)},$$

and $$\Delta = \Phi_1-\Phi_2-(\Phi_1'-\Phi_2'),$$

where Φ is the same as on p. 308 and Φ' is obtained from Φ by putting $Q = 1$ and $\psi = 0$.

From these formulæ and the constants already set out we derive the following set of values for the difference of phase in the case of *Silver*:—

e_1/λ.	$\phi = 20°$.	40°.	60°.	75°.	80°.	85°.
0·001	0·0019	0·0064	0·0177	0·0546	0·0791	0·1423
0·005	0·0085	0·0286	0·0978	0·2179	0·2923	0·3930
0·01	0·0154	0·0664	0·1644	0·3167	0·3941	0·5009
0·02	0·0170	0·0915	0·2166	0·3834	0·4778	0·6181
0·05	0·0220	0·0939	0·2328	0·4328	0·5658	0·7201
0·1	0·0208	0·0904	0·2296	0·4667	0·5939	0·7484
0·2	0·0207	0·0900	0·2295	0·4679	0·5973	0·7513

These results are represented in figs. 13 and 14 below.

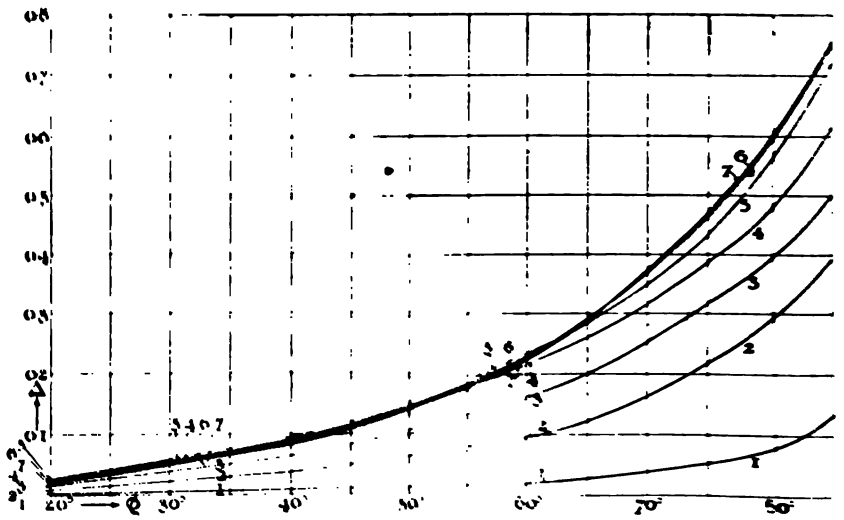


FIG. 13.

Fig. 13 shows the difference of phase (Δ) as a function of the angle of incidence (ϕ). The difference of phase increases with the incidence, at first slowly, but afterwards rapidly, especially when the thickness of the plate is not very small. The next figure (14) indicates more clearly in what way Δ depends on the thickness. For incidences up to 60°, Δ increases fairly rapidly

at first, then more slowly until a maximum is reached, and then declines very slowly to the value appropriate to a thick plate. For larger incidences the increase of Δ is much more rapid at first, and the increase continues throughout, although as the thickness increases it becomes very slow, until it reaches the value corresponding to a thick plate. As no very careful measurements have been made for transmission through silver,* we cannot test these results by comparing them with experiment.

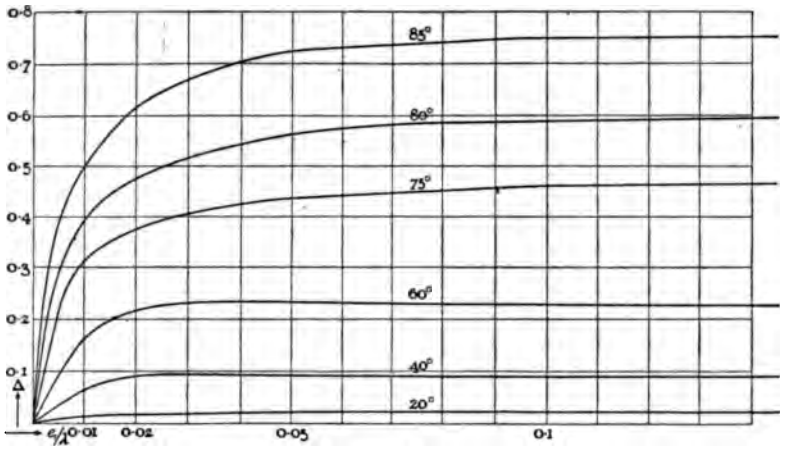


FIG. 14.

In the azimuth (ω) we get the following table:—

e_1/λ.	ϕ = 20°.		40°.		60°.		75°.		80°.		85°.	
	°	′	°	′	°	′	°	′	°	′	°	′
0·001	45	1	45	6	45	19	45	43	45	49	53	36
0·005	45	14	45	59	48	7	54	0	58	59	72	17
0·01	45	40	47	52	53	17	63	51	69	53	79	47
0·02	46	36	51	41	61	44	73	37	78	5	83	44
0·05	47	51	56	36	70	23	80	29	82	55	85	28
0·1	48	10	57	51	72	19	81	48	83	44	85	42
0·2	48	12	57	58	72	31	81	54	83	48	85	43

These results are represented in figs. 7 and 8 above. The azimuth is always greater than 45°. It increases slowly and almost uniformly as the incidence increases, except for large values of ϕ, when the increase is more rapid, especially for very thin films. The azimuth also increases with the thickness, very rapidly at first, especially for large values of ϕ; but after the thickness is greater than 0·05 λ the increase is very slow.

* Meslin made a few such measurements, but did not record the thickness of the silver. His experiments with gold will come under discussion later.

Similar results are obtained for *gold* with the constants already set out. In this way we get the following table for the difference of phase (Δ).

e_1/λ.	$\phi = 30°$.	40°.	50°.	60°.	70°.	80°.	85°.
0·001	0·0055	0·0239	0·0384	0·0482	0·0442	0·0409	0·0406
0·005	0·0101	0·0445	0·0712	0·0898	0·0833	0·0779	0·0776
0·01	0·0171	0·0743	0·1167	0·1460	0·1390	0·1311	0·1317
0·02	0·0280	0·1180	0·1805	0·2231	0·2262	0·2214	0·2218
0·05	0·0547	0·2300	0·3143	0·3874	0·4260	0·4361	0·4417
0·1	0·0992	0·3125	0·4140	0·5141	0·6371	0·6778	0·6837
0·2	0·1812	0·4881	0·5554	0·6775	0·7848	0·8112	0·8156

These results are set out graphically in fig. 15 below.

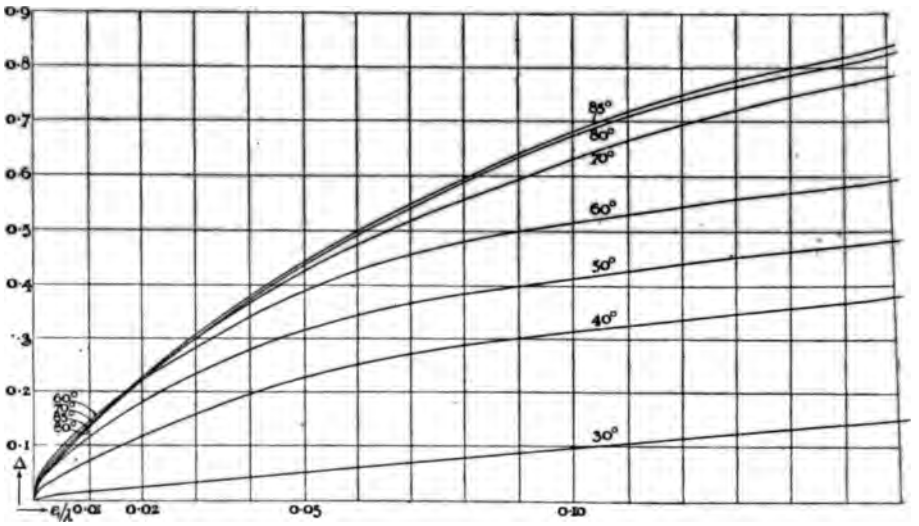


FIG. 15.

On comparing this with fig. 14 above, we see that although the general trend is the same for both metals, there are some important differences. With silver the difference of phase increases with the angle of incidence for all thicknesses. This is the case also with gold for thicknesses greater than $0{\cdot}02\,\lambda$. However, for thinner films than this, Δ diminishes when ϕ is greater than 60°. With silver we have seen that for certain angles of incidence Δ increases for a time, reaches a maximum, and then slowly declines. With gold, on the other hand, Δ seems always to increase with the thickness. The increase too, is not nearly so rapid as in the case of silver, and even when $\epsilon = 0{\cdot}2\,\lambda$ we see that Δ has not yet reached a steady value.

The following table gives the values of the azimuth (ω):—

e_1/λ.	ϕ = 30°.	40°.	50°.	60°.	70°.	80°.	85°.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′
0·001	45 8	45 14	45 24	45 37	46 0	48 0	52 21
0·005	46 1	46 50	48 10	50 20	54 20	63 56	73 42
0·01	47 25	49 26	52 28	56 54	63 34	73 45	80 8
0·02	49 52	53 47	59 17	66 7	73 5	80 14	83 8
0·05	52 43	58 42	66 8	73 54	80 21	83 57	84 18
0·1	53 30	60 3	67 56	75 55	81 58	84 14	84 24
0·2	53 37	60 14	68 11	76 9	82 9	84 15	84 24

These results are represented in fig. 12 above, and on comparison with fig. 7 we see that there is very little difference between the two metals as regards the law of variation of the azimuth.

Influence of the Transition Layer.

So far we have proceeded on the hypothesis that the transition from one medium to another is abrupt and not gradual. This neglect of the layer of transition has led us to results that agree quite as well as could be expected with experiment. Unfortunately, however, the experiments that we have been able to quote are all too few in number.* They deal almost exclusively with observations of the Principal Incidence and Azimuth, and even for these the observations extend over a rather narrow range of thickness of the metallic film. We shall now turn, however, to a much more extensive series of experiments giving us the difference of phase for reflection and transmission over a wide range of thicknesses.† These experiments were made with leaves of gold and we have already (p. 318) been led to expect that for this metal the influence of the transition layer on the difference of phase would be more appreciable than with silver. When we examine Meslin's results for reflection from a *thick* plate of gold we find that the theory of an abrupt transition will not give us results that agree even approximately (except in a very rough way) with the facts of experience. It is known that on such a theory the difference of phase is given by the formula

$$\tan \Delta = \frac{2Mc \cos\phi \sin^2\phi \sin(\alpha+u)}{M^2c^2\cos^2\phi - \sin^4\phi},$$

and the Principal Incidence by the formula‡

$$\frac{\sin^2\phi}{\cos\phi} = Mc, \quad \text{or its equivalent,} \quad \sec\phi = M + M^{-1}(1-\tfrac{1}{2}\cos 2\alpha).$$

* It would be a great advantage if we could obtain accurate measurements of the difference of phase and the azimuth for both reflection and transmission. Meslin gives us the difference of phase, but not the azimuth.

† See note §, p. 296.

‡ See 'Roy. Soc. Proc.,' 1906, pp. 213 and 215.

Meslin found the Principal Incidence to be 74°, and as $1-\frac{1}{2}\cos 2\alpha$ must lie between 0·5 and 1·5, we see that M must lie between 3·15 and 3·49. When the incidence was 30°, Meslin found $\Delta = 11° 31'$, and from the formula for Δ we see that M cannot be greater than 2·8. This lies considerably outside the limits for M fixed by the Principal Incidence and we should be led to a similar inconsistency if we considered the value of Δ at any other incidence than that of 30°. The crosses in fig. 16 below represent Meslin's values of Δ for different incidences and it will be seen that they are very

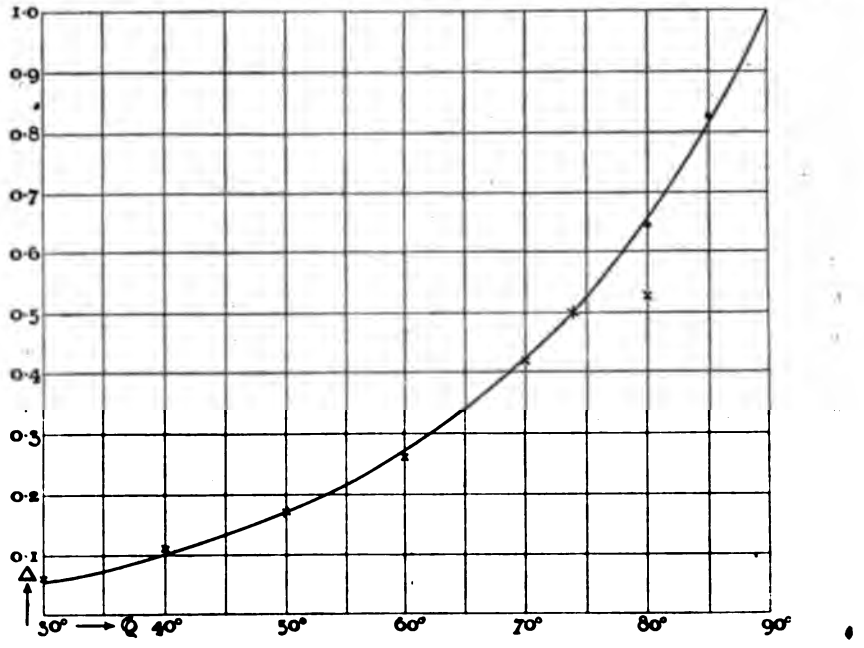


FIG. 16.

fairly consistent.* The continuous curve of the figure represents the theoretical results obtained later when the layer of transition is considered.

We proceed to develop some formulæ applicable to the problem when the transition layer is taken into account. In that case in addition to the optical constants, M and α, two new constants a and w are required whose values depend on the law of variation of μ within the layer. The quantities hitherto

* At least up to $\phi = 74°$. There is evidently a misprint in the values of Δ given for $\phi = 80°$ and 85°. They are set down as 0·528 and 0·648 respectively. An inspection of the figure shows that these are quite inconsistent with the other results and with the graph given by Meslin. Probably the numbers should be 0·648 and 0·828, 5 being replaced by 8, and the two values interchanged. Owing to the uncertainty of these results they have been neglected altogether in the subsequent determination of the optical constants of the gold.

represented by r_1 and r_2 are replaced by r_1' and r_2', which are given by the following equations* :—

$$r_1' = \frac{\sin(\phi-\phi')\cos(\phi+\phi')+ae^{iw}\sin\phi'\cos\phi'\cos\phi}{\sin(\phi+\phi')\cos(\phi-\phi')+ae^{iw}\sin\phi'\cos\phi'\cos\phi}$$

$$= \frac{A+a'}{A'+a'}, \text{ say, } = \frac{A}{A'}\left[1+a'\left(\frac{1}{A}-\frac{1}{A'}\right)\right], \text{ approximately}$$

$$= r_1\left[1+a'\left(\frac{1}{A}-\frac{1}{A'}\right)\right] = r_1[1+p_1e^{i\lambda_1}],$$

where

$$p_1e^{i\lambda_1} = a'\left(\frac{1}{A}-\frac{1}{A'}\right) = \frac{2ae^{iw}\sin^2\phi'\cos^2\phi'\cos\phi}{\sin(\phi+\phi')\cos(\phi+\phi')\sin(\phi-\phi')\cos(\phi-\phi')}.$$

$$r_2' = -\frac{\sin(\phi-\phi')+ae^{iw}\sin\phi'}{\sin(\phi+\phi')+ae^{iw}\sin\phi'} = \frac{B+b'}{B'+b'} = r_2[1+p_2e^{i\lambda_2}],$$

where

$$p_2e^{i\lambda_2} = b'\left(\frac{1}{B}-\frac{1}{B'}\right) = \frac{2ae^{iw}\sin^2\phi'\cos\phi}{\sin(\phi+\phi')\sin(\phi-\phi')},$$

$$\frac{r_1'}{r_2'} = \frac{r_1}{r_2}(1+q_1e^{i\theta}) = s\frac{R_1}{R_2}e^{-i(\delta-\chi_1)},\dagger$$

$$s = (1+2q_1\cos\theta+q_1^2)^{\frac{1}{2}}, \quad \tan\chi_1 = \frac{q_1\sin\theta}{1+q_1\cos\theta}, \quad \theta = 2\alpha+w+\theta',$$

$$q_1 = \frac{2a\sin^2\phi\cos\phi}{[M^4\cos^4\phi+c^4-2M^2c^2\cos^2\phi\cos 2(\alpha-u)]^{\frac{1}{2}}};$$

$$\tan\theta' = \frac{c^2\sin 2(\alpha-u)}{M^2\cos^2\phi-c^2\cos 2(\alpha-u)}.$$

δ is the difference of phase that an abrupt transition would produce, and is given by the formula for Δ on p. 325, while χ is the correction due to the transition layer.

Since q_1 and θ must be calculated in order to determine χ_1, it will be convenient to express p and λ in terms of these quantities. From the above formulæ we have

$$p_1e^{i\lambda_1} = q_1e^{i\theta}\frac{\cos^2\phi'}{\sin^2\phi} = q_1\frac{c^2e^{i(\theta-2u)}}{\sin^2\phi},$$

whence

$$p_1 = q_1c^2/\sin^2\phi \quad \text{and} \quad \lambda_1 = \theta-2u.$$

Similarly

$$p_2e^{i\lambda_2} = q_1e^{i\theta}\frac{\cos(\phi+\phi')\cos(\phi-\phi')}{\sin^2\phi} = \frac{q_1e^{i\theta}}{\sin^2\phi}[\cos^2\phi'-\sin^2\phi]$$

$$= \frac{q_1e^{i\theta}}{\sin^2\phi}[c^2e^{-i2u}-\sin^2\phi],$$

* See 'Roy. Soc. Proc.,' 1906, p. 222.

† *Ibid.*, p. 222—3. χ has been replaced by χ_1 and q by q_1 to avoid confusion with the quantity called q in the earlier part of this paper. The quantity q is printed with the wrong sign in the paper referred to, and θ and θ' of p. 224 should each be increased by 180°.

whence

$$p_2 = \frac{q_1}{\sin^2\phi}(c^4+\sin^4\phi-2c^2\sin^2\phi\cos 2u)^{\frac{1}{2}} = \frac{q_1c^2}{\sin^2\phi}\cdot\frac{\sin 2u}{\sin\Omega} = p_1\frac{\sin 2u}{\sin\Omega},$$

and

$$\lambda^2 = \theta-\Omega,$$

where

$$\tan\Omega = \frac{c^2\sin 2u}{c^2\cos 2u-\sin^2\phi}.$$

It thus appears that there will be no great difficulty in calculating all the quantities involved in our formulæ, once the four optical constants M, α, a, and w are obtained. However, to obtain these four quantities *accurately* from a series of observations of the difference of phase ($\delta - \chi_1$) at different angles of incidence is a problem involving some labour. Theoretically, we could obtain the four constants from any four observations of $\delta - \chi_1$; but the equations are much too complicated to be solved as a set of four simultaneous equations. Practically we must proceed by a series of approximations and in this way consistent results are soon obtained, unless very great accuracy is aimed at. From the formulæ it appears that χ_1 (the correction to the change of phase due to the layer) vanishes at normal incidence and is small when the angle of incidence is small. We can, therefore, obtain a first approximation to M and α from two observations of the difference of phase when the angle of incidence is not large. As a first approximation in such circumstances we can neglect χ_1 altogether, or give to it any small value that seems reasonable. Knowing M and α (approximately) we can calculate δ, q_1/a, and θ' from the formulæ above. Having obtained δ by calculation, and $\delta - \chi_1$ from observation for any other angle of incidence, we thus obtain χ_1 for that incidence. Also we have

$$\tan\chi_1 = \frac{q_1\sin\theta}{1+q_1\cos\theta},$$

so that

$$\frac{1}{a} = \frac{q_1}{a}\frac{\sin(\theta-\chi_1)}{\sin\chi_1} = \frac{q_1}{a}\frac{\sin(w+2\alpha+\theta'-\chi_1)}{\sin\chi_1}.$$

In this equation everything is known (approximately) except a and w, so that by using our knowledge of $\delta - \chi$ at two angles of incidence, other than those employed for obtaining the approximate values of M and α, we easily obtain the unknown quantities a and w. Having thus obtained approximate values of the four optical constants, we can calculate χ in terms of them, and proceed, if necessary, to higher approximations. If the experimental results give us the difference of phase for more than four angles of incidence, we can use the ordinary rules for finding the most probable values of the optical constants, and estimate the probable errors.

In carrying out the process sketched above with reference to any set of

observations actually available at present, we find that the approximations need not be carried very far, for we soon obtain results that fit in with experiment well within the limits of experimental errors. We take Meslin's results with red light reflected from gold; and the second approximation in the above process yields the following values of the optical constants:— $M = 2{\cdot}63$; $\alpha = 70°$; $a = 0{\cdot}7$; $w = 70°\ 39'$. From these we derive the following table, giving the values of χ, $\Delta\,(=\delta - \chi_1)$, and the difference between theory and observation:—

ϕ.	30°.	40°.	50°.	60°.	70°.	74°.	80°.	85°.
χ_1	0·009	0·017	0·027	0·041	0·055	0·061	0·051	0·027
Δ (calculated) ...	0·056	0·103	0·176	0·270	0·423	0·5	0·663	0·815
Δ (observed).....	0·064	0·112	0·176	0·260	0·420	0·5	0·648	0·828
Difference ...	−0·008	−0·009	0	+0·010	+0·003	0	+0·015	−0·013

These results are represented in fig. 16 above, in which the continuous curve corresponds to the theory and the crosses to the experiment. From the figure or the table we see that the agreement between theory and experiment is a close one, and that, in view of the uncertainty as to some of the experimental results, not much could be gained by proceeding to a higher approximation. We shall therefore take the constants given above as the basis of our calculations. From the formulæ already given we then derive the following table:—

ϕ.	30°.	40°.	50°.	60°.	70°.	80°.
u	0° 38′	1° 3′	1° 25′	1° 50′	2° 8′	2° 20′
c	1·014	1·023	1·032	1·042	1·047	1·054
$180-\theta_1$	46° 5′	51° 56′	61° 4′	75° 46′	99° 28′	135° 23′
$180-\theta_2$	34° 25′	30° 22′	25° 22′	19° 44′	13° 29′	6° 50′
R_1^2	0·5861	0·5505	0·5105	0·3720	0·3857	0·4196
R_2^2	0·6738	0·7079	0·7504	0·7834	0·8602	0·9270
m	2·667	2·690	2·716	2·742	2·760	2·773
χ	70° 39′	71° 3′	71° 28′	71° 50′	72° 8′	72° 20′
ψ	63° 36′	62° 55′	62° 10′	61° 32′	60° 58′	60° 37′
Log Q	2·626	2·610	2·594	2·578	2·566	2·558
$\lambda_1 - 360°$	35° 47′	36° 49′	39° 5′	43° 34′	52° 4′	63° 24′
$\lambda_2 - 360°$	35° 23′	35° 27′	35° 38′	35° 26′	35° 38′	33° 14′
p_1	0·2076	0·2297	0·2606	0·2894	0·2974	0·2830
p_2	0·1578	0·1392	0·1177	0·0905	0·0621	0·0401

We are now in a position to discuss all the problems dealt with in the earlier part of this paper without neglecting the layer of transition from one medium to another. The effect of this layer is to replace by $r(1 + pe^{i\Delta})$. The other quantities remain as before, but it must be

remembered that q on pp. 297 *et seq.* refers to a thickness t_1 of *homogeneous* metal. We shall set out our results in terms of t_1, but, of course, this is not the actual thickness of the plate. To get that thickness we must increase t_1 by twice the thickness of the layer, and it is owing to the uncertainty as to the value of this latter quantity that we cannot state the results precisely in terms of the thickness of the metallic plate. If d be the thickness of the layer we should expect* $2\pi d/\lambda$ to lie between a/M^4 and a/M^2, and with the constants given above this makes d/λ lie between 0·0023 and 0·0161.†

If light be incident normally on a gold leaf whose optical constants are those just determined, then the intensity and change of phase for the reflected and transmitted light are as follows :—

e_1/λ.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.
R^2 (reflection)	0·001	0·023	0·079	0·234	0·660	0·870	0·861
R^2 (transmission)...	0·933	0·845	0·736	0·547	0·218	0·049	0·002
θ' (reflection)	0·655	0·678	0·700	0·739	0·791	0·815	0·800
θ' (transmission) ...	0·001	0·013	0·056	0·079	0·106	0·068	−0·101

These results are represented graphically in Curve 3 of figs. 1, 2, 3 and 4, above.

If the gold, instead of being surrounded by air, is deposited on glass, these results must be modified as in the case of silver on p. 305. The intensity and change of phase for the reflected light are then given by the following table :—

e_1/λ.	0·001.	0·005.	0·01.	0·02.	0·05.	0·1.	0·2.
R_1^2	0·035	0·030	0·077	0·219	0·644	0·860	0·860
θ'	0·081	0·307	0·509	0·662	0·776	0·815	0·800

* See 'Roy. Soc. Proc.,' 1906, p. 229. With the law of variation of μ^2 given on p. 230, we have, for the gold alone, $E_1 = 2{\cdot}228$. This makes $d/\lambda = 0{\cdot}007$, which is about half way between the limits found in the text, and is almost identical with the value obtained for the layer of transition in the case of reflection from diamond. See 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 63.

† That so thin a layer should produce an appreciable change in the Principal Incidence and Azimuth is not altogether surprising after what has been seen on p. 315. The gold under discussion here is a good example of the error that may be made in deriving the optical constants of a metal from observations of the Principal Incidence and Azimuth and neglect of the transition layer. The Principal Incidence is 74° and the Principal Azimuth, obtained from the formula $\tan\beta = R_1 R_2 . (1+2q_1\cos\theta+q_1^2)^{\frac{1}{2}}$, is 44° 57′. Neglecting the layer of transition these would give $M = 3{\cdot}316$ instead of $M = 2{\cdot}63$ and $\alpha = 87°\ 40'$ instead of $\alpha = 78°$. If $M e^{-i\alpha} = \mu_1 - i\alpha_1$, then we should get $\mu_1 = 0{\cdot}135$, instead of $\mu_1 = 0{\cdot}9$ and $\alpha_1 = 3{\cdot}31$ instead of $\alpha_1 = 2{\cdot}47$.

These results are exhibited in Curve 6 of figs. 1 and 2 above. From the first of these figures we see, by comparing Curves 1 and 4, or 2 and 5, that for silver or gold and an abrupt transition the intensity of the reflected light is always greater for the metal deposited on glass than for the metal plate alone. The difference between the two cases is, however, small, and tends to zero as the thickness increases. On comparing Curves 3 and 6 we see that in this respect the layer of transition modifies the results considerably. After a thickness $t_1 = 0{\cdot}001\,\lambda$ has been reached, the intensity of the light reflected from gold on glass is *less* than that reflected from gold alone.

To determine the ellipticity difference of phase when the light is incident at any angle ϕ we have to modify the formulæ on p. 308 by replacing r by $r' = r(1 + pe^{i\lambda})$. For the reflected light we have

$$\frac{R_1'}{R_2'} e^{i(\theta_1' - \theta_2')} = \frac{r_1'}{r_2'} \frac{(1 - q_1^2 r_2'^2)}{(1 - q_1^2 r_1'^2)},$$

where

$$\frac{r_1'}{r_2'} = \frac{r_1}{r_2}(1 + q_1 e^{i\theta}) = s \frac{R_1}{R_2} e^{-i(\delta - \chi_1)} \quad \text{and} \quad s = (1 + 2q_1 \cos\theta + q_1^2)^{\frac{1}{2}}.$$

$$1 - q_1^2 r'^2 = 1 - QR^2 e^{i(2\theta - \psi)}(1 + 2pe^{i\lambda}) \text{ approximately,}$$

$$= [1 - QR^2 \{\cos(\psi + \gamma) + 2p\cos(\psi + \gamma - \lambda)\}] + iQR^2 \{\sin(\psi + \gamma) + 2p \sin(\psi + \gamma - \lambda)\},$$

where $\gamma = 360° - 2\theta$.

Thus $1 - q_1^2 r'^2 = Ae^{i\Phi}$, where A and Φ are the modulus and argument respectively of the complex quantity.

$$1 - QR^2 \{\cos(\psi + \gamma) + 2p\cos(\psi + \gamma - \lambda)\} + iQR^2 \{\sin(\psi + \gamma) + 2p \sin(\psi + \gamma - \lambda)\}.$$

The difference of phase is

$$\Delta = \theta_2' - \theta_1' = \delta - \chi_1 + \Phi_1 - \Phi_2,$$

and the ellipticity is

$$\epsilon = \tan\omega = \frac{sR_2}{R_1} \frac{A_2}{A_1}.$$

From these formulæ we get the following table for Δ:—

e_1/λ.	ϕ = 30°.	40°.	50°.	60°.	70°.	80°.
0·001	0·112	0·205	0·341	0·524	0·795	1·195
0·005	0·103	0·188	0·311	0·477	0·718	1·052
0·01	0·094	0·170	0·283	0·433	0·652	0·965
0·02	0·081	0·147	0·246	0·380	0·579	0·865
0·05	0·067	0·127	0·206	0·317	0·492	0·743
0·1	0·060	0·109	0·185	0·283	0·440	0·679
0·2	0·057	0·103	0·176	0·271	0·424	0·664

These results are represented in fig. 17 below.

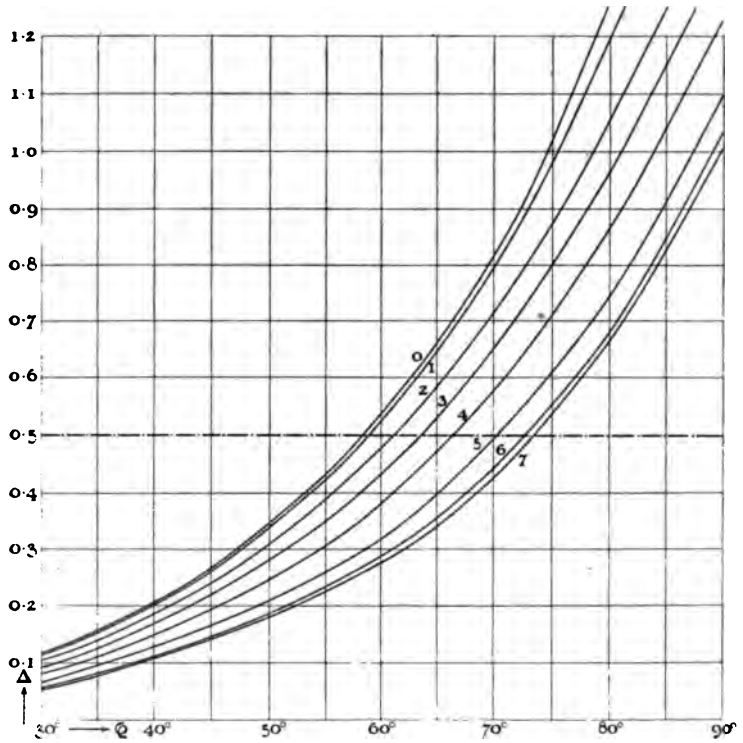


FIG. 17.

A comparison of this figure with fig. 11 above will indicate the nature of the modifications introduced by the layer. As far as the variation of Δ with change of ϕ for any given thickness is concerned, there is not any very marked difference between the two figures. The main difference lies in the variation due to change of thickness. When the layer is taken into account, Δ always diminishes with the thickness; but without the layer this is not always the case. It will be seen, too, that Curves 5, 6, 7 of fig. 11 are much more crowded than the corresponding curves of fig. 17. Without the layer there is very little change in Δ for thicknesses greater than $0{\cdot}05\,\lambda$; but with the layer there is still a considerable change after ϵ_1 has passed that value.

The Principal Incidence corresponding to each thickness is obtained from the graph. It increases steadily with the thickness, its values being 58° 20′, 58° 48′, 61° 10′, 63° 40′, 66° 18′, 70° 15′, 72° 40′, and 73° 30′.

If the incident light be of unit intensity and be polarised in a plane making an angle of 45° with the plane of incidence, then the intensity of the reflected light is given by the formula

$$I = \tfrac{1}{2}(R_1'^2 + R_2'^2).$$

We have $$r' = r(1+pe^{i\lambda}) = ae^{i\alpha},$$

where $a = (1+2p\cos\lambda+p^2)^{\frac{1}{2}}$ and $\tan\alpha = p\sin\lambda/(1+p\cos\lambda)$.

$$1-q^2r'^2 = Ae^{i\Phi};\quad 1-q^2 = 1-Qe^{-i\psi} = be^{i\beta},$$

where $b = (1-2Q\cos\psi+Q^2)^{\frac{1}{2}}$ and $\tan\beta = Q\sin\psi/(1-Q\cos\psi)$.

Whence $$R'e^{i\theta'} = \frac{r'(1-q^2)}{1-q^2r'^2} = \frac{abR}{A}e^{i[\theta+\alpha+\beta-\Phi]}.$$

Thus $$R' = abR/A \quad \text{and} \quad \theta' = \theta+\alpha+\beta-\Phi.$$

From these formulæ we derive the following values of I:—

e_1/λ =	0·001	0·005	0·01	0·02	0·05	0·1	0·2
30°	0·001	0·017	0·065	0·192	0·528	0·773	0·836
40	0·001	0·018	0·071	0·203	0·537	0·772	0·845
50	0·001	0·026	0·083	0·223	0·547	0·770	0·829
60	0·002	0·035	0·109	0·252	0·570	0·760	0·783
70	0·005	0·063	0·162	0·325	0·604	0·800	0·838
80	0·014	0·171	0·295	0·457	0·665	0·817	0·857

These results are represented in fig. 18 below.

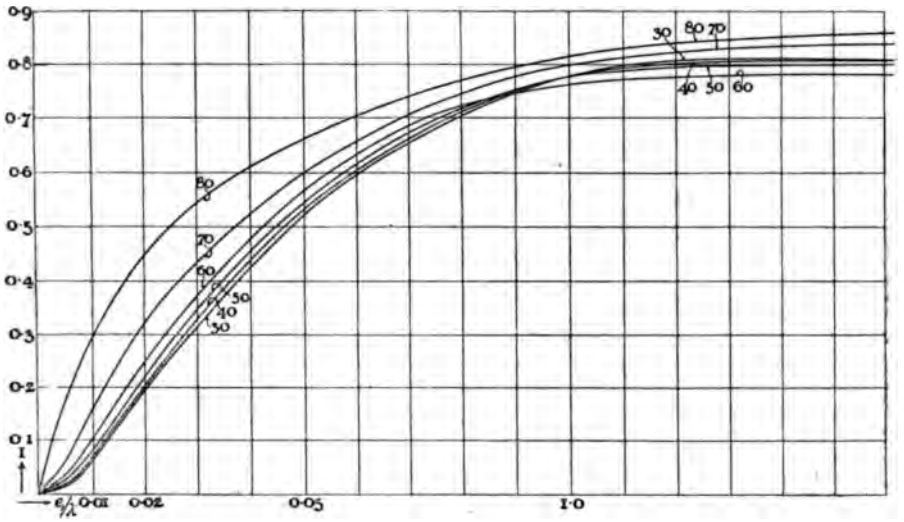


Fig. 18.

For thicknesses less than 0·08 λ the intensity increases with the angle of incidence, but for greater thicknesses the intensity obeys a different law. The law approaches more and more closely to that for a thick plate, the intensity diminishing slightly until the "quasi-polarising" angle is reached and then increasing towards unity as the angle of incidence tends towards 90°.

For the Azimuth (ω) we get the following set of values:—

e_1/λ.	$\phi = 30°$.		40°.		50°.		60°.		70°.		80°.	
	°	′	°	′	°	′	°	′	°	′	°	′
0·001	37	46	32	5	25	10	17	34	11	25	6	38
0·005	38	14	32	55	26	25	19	5	13	17	9	16
0·01	38	55	34	7	28	11	21	16	16	7	13	48
0·02	40	11	36	24	31	42	26	44	21	45	20	54
0·05	42	41	40	49	38	31	35	10	32	16	32	38
0·1	43	51	43	41	42	0	39	21	37	15	36	3
0·2	44	7	43	24	42	30	39	41	37	35	36	4

These results are represented in fig. 19 below, in which the crosses indicate the position of the Principal Incidence and the Principal Azimuth.

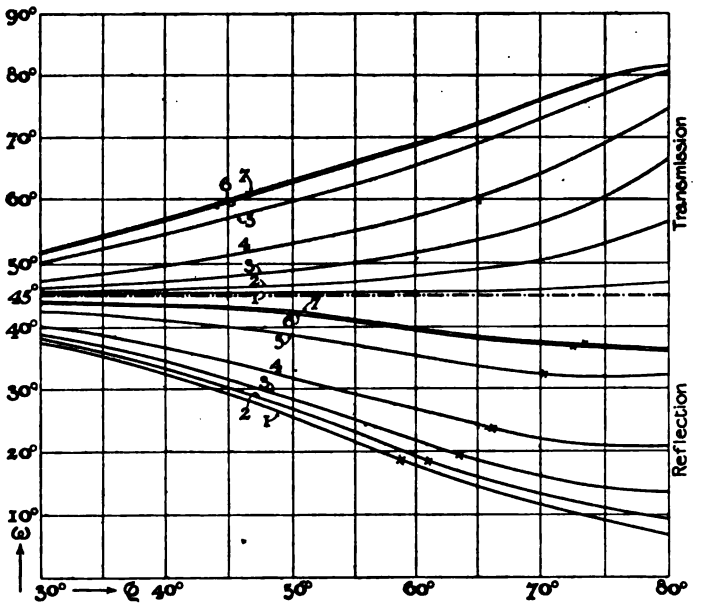


Fig. 19.

A comparison with fig. 12 will show that the influence of the layer of transition on the law of variation of the ellipticity is very slight.

Turning to the transmitted beam, we proceed as on pp. 321 and 322, and find that the difference of phase and the ellipticity are given by the formulæ

$$\Delta = \Phi_1 - \Phi_2 - (\Phi_1' - \Phi_2') \quad \text{and} \quad \epsilon = \tan\omega = \frac{A_2}{A_1}\frac{A_1'}{A_2'},$$

where A and Φ have the same values as on p. 331, while A′ and Φ' are derived from them by putting $Q = 1$ and $\psi = 0$.

From these we get the following table for Δ:—

e_1/λ.	ϕ = 30°.	40°.	50°.	60°.	70°.	80°.
0·001	0·004	0·005	0·008	0·013	0·025	0·062
0·005	0·013	0·022	0 038	0·060	0·102	0·195
0·01	0·023	0·040	0·067	0·104	0·167	0·282
0·02	0·035	0·063	0·103	0·157	0·241	0·382
0·05	0·049	0·083	0·143	0·220	0·328	0·503
0·1	0·057	0·101	0·165	0·254	0·379	0·567
0·2	0·059	0·107	0·173	0·267	0·395	0·583

Fig. 20 below represents these results graphically.

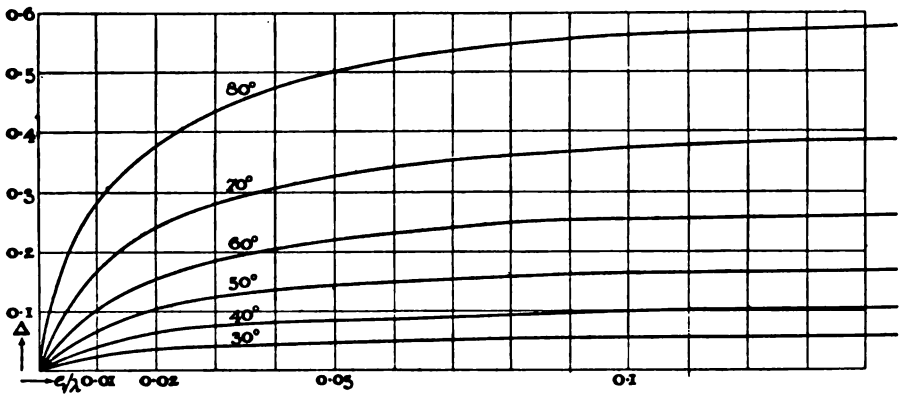


Fig. 20.

A comparison with fig. 15 shows that the layer of transition modifies the law of variation of Δ to some extent. The curves in fig. 20 correspond more closely to those for silver in fig. 14 than to those for gold in 15. The difference of phase always increases with the incidence and as the thickness increases it soon reaches a steady value. This was not the case with homogeneous gold (see p. 324). It should be noted, too, that though the principal optical constants M and α are not very different for the two specimens of gold that have been considered, the numerical values of Δ are appreciably different in the two cases. Hence to get a close numerical agreement between theory and experiment the optical constants would have to be determined accurately.

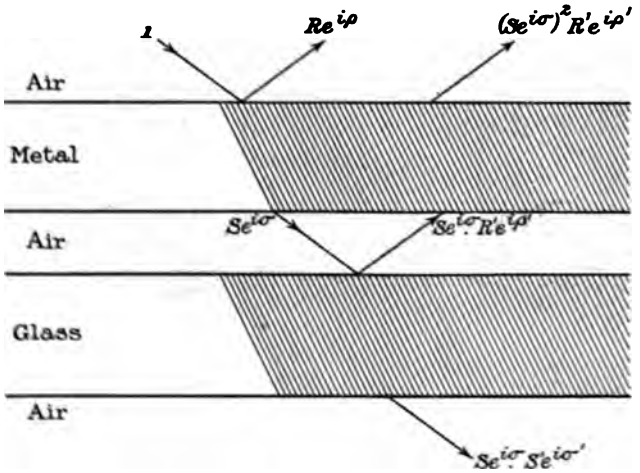
The azimuth is given in the table on p. 336.

Fig. 19 above represents these results and a comparison with fig. 12 will show that the azimuth is little affected by the layer of transition—as we found was the case with the reflected beam also.

Before we can compare these results with Meslin's experiments we must ascertain to what extent they are modified when the gold is deposited on glass

instead of being surrounded by air. This can be done most simply by the method described on p. 306 above.

e_1/λ.	ϕ = 30°.	40°.	50°.	60°.	70°.	80°.
	° ′	° ′	° ′	° ′	° ′	° ′
0·001	45 6	45 10	45 20	45 35	45 58	46 57
0·005	45 34	46 5	46 56	48 6	50 22	56 21
0·01	46 16	47 23	49 6	51 26	55 55	66 8
0·02	47 34	49 47	53 4	57 2	63 52	74 8
0·05	50 4	54 11	59 45	65 10	72 48	80 18
0·1	51 18	56 18	62 43	68 14	75 35	81 31
0·2	51 29	56 37	63 8	68 33	75 45	81 32



A beam of unit amplitude incident on the metal gives rise to a reflected beam $Re^{i\rho}$ and a transmitted beam $Se^{i\sigma}$, where, as we have seen,

$$Re^{i\rho} = \frac{r(1-q^2)}{1-q^2r^2} \quad \text{and} \quad Se^{i\sigma} = \frac{q(1-r^2)}{1-q^2r^2}.$$

The beam $Se^{i\sigma}$ is then incident on a glass plate and gives rise to a reflected beam $Se^{i\sigma}.R'e^{i\rho'}$ and a transmitted beam $Se^{i\sigma}.S'e^{i\sigma'}$. Here

$$R'e^{i\rho'} = \frac{r'(1-q'^2)}{1-q'^2r'^2} \quad \text{and} \quad S'e^{i\sigma'} = \frac{q'(1-r'^2)}{1-q'^2r'^2},$$

where r' is obtained from Fresnel's formulæ for reflection and $q' = e^{-\frac{2\pi\mu'}{\lambda}\sec\phi'}$, where μ' is the coefficient of reflection and e' is thickness of the glass.

The wave $Se^{i\sigma}R'e^{i\rho'}$ reflected from the glass is transmitted through the metal plate and gives rise to a wave $(Se^{i\sigma})^2R'e^{i\rho'}$ in the air. Thus the transmitted

wave is $SS'e^{i(\sigma+\sigma')}$ and the reflected wave is the resultant of $Re^{i\rho}$ and $(Se^{i\sigma})^2R'e^{i\rho'}$.

These results are quite general and would suffice to solve the problem in the most complicated case when both plates (metal and glass) were thin, *i.e.*, not large compared with a wave-length. In the problem at present in hand the glass plate is thick, and under these circumstances there is a considerable simplification. We then have $S'e^{i\sigma'} = q'$ and $R'e^{i\rho'} = r'$, so that the transmitted beam is $q'Se^{i\sigma}$ and the reflected one is the resultant of $Re^{i\rho}$ and $r'(Se^{i\sigma})^2$.

The transmitted wave is most readily disposed of. The effect of the glass is to replace $Se^{i\sigma}$ by $q'Se^{i\sigma}$. The factor q' is the same whether the light be polarised parallel or perpendicularly to the plane of incidence. Hence the glass has no influence on the *difference* of phase nor on the ellipticity of the transmitted beam. We should expect, then, that the results on p. 334 above should agree, within the limits of experimental error, with Meslin's values. A comparison shows that there is a very fair agreement as far as the law of variation of Δ is concerned. Owing to the uncertainty as to the thickness of the layer of transition and the difficulty of obtaining accurate measurements of the thickness of the metallic deposit, we cannot compare the numerical results of theory and experiment with much hope of an exact equivalence. As we shall see later, the experiments on reflection, when compared with theory, give us a fair basis of comparison as far as thickness is concerned. On determining in this way the thicknesses to be compared, it appears that the theoretical results, although obeying much the same law of dependence on ϕ as Meslin's values, are uniformly higher than these values. However, as was observed on p. 335 above, a slight change in the optical constants makes an appreciable difference in the difference of phase of the transmitted light—and in view of this fact the agreement between theory and experiment is as close as could be expected. Unfortunately, Meslin made no record of the ellipticity, so that we have no means of comparison in this region.

The reflected light is the resultant of $Re^{i\rho}$ and $r'(Se^{i\sigma})^2$. Denoting this by $R'e^{i\theta'}$, we have

$$R'^2 = R^2 + r'^2S^4 + 2r'RS^2(\rho - 2\sigma),$$

and

$$\tan\theta' = \frac{R\sin\rho + r'S^2\sin 2\sigma}{R\cos\rho + r'S^2\cos 2\sigma}.$$

The difference of phase Δ is given by

$$\Delta = \theta_2' - \theta_1',$$

and the ellipticity (ϵ) by

$$\epsilon = \tan\omega = R_1'/R_2'.$$

The quantities R and ρ of these formulæ are identical with R′ and θ' of p. 333; *i.e.*, $R = abR/A$ and $\rho = \theta+\alpha+\beta-\Phi$. To determine S and σ we have

$$Se^{i\sigma} = \frac{q(1-r^2)}{1-q^2r'^2} = \frac{Q^{\frac{1}{2}}e^{-\frac{1}{2}i\psi}A'e^{i\Phi'}}{Ae^{i\Phi}}.$$

Hence $S^2 = Q(A'/A)^2$ and $\sigma = \Phi'-\Phi-\frac{1}{2}\psi$.

The only other quantity involved is r'. This is given by Fresnel's formulæ. This, of course, involves the index of refraction of the glass, and this, unfortunately, Meslin did not put on record. In our calculations we shall take $\mu' = 1{\cdot}54$, which corresponds to a polarising angle of 57°.

The following table gives the values of R_1':—

	$e_1/\lambda = 0{\cdot}01$.	0·02.	0·05.	0·1.	0·2.
°					
30	0·221	0·385	0·687	0·854	0·899
40	0·200	0·362	0·667	0·843	0·897
50	0·179	0·338	0·638	0·812	0·857
60	0·180	0·316	0·573	0·723	0·749
70	0·278	0·379	0·618	0·743	0·750
80	0·529	0·599	0·756	0·842	0·850

These results are represented in fig. 21 below.

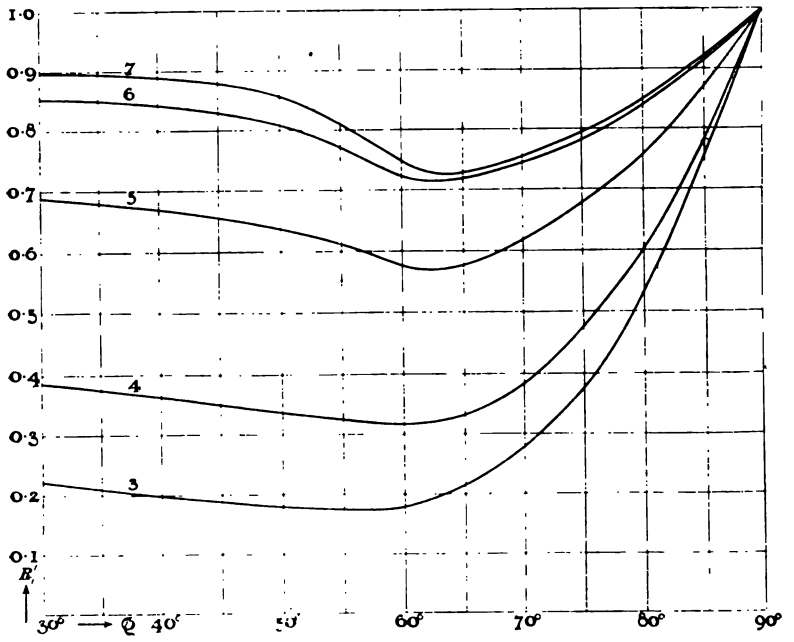


FIG. 21.

R_1' increases rapidly with the thickness. It diminishes as the incidence increases, reaches a minimum, and then increases to unity. The "quasi-polarising" angle—*i.e.*, the angle of incidence that makes R_1' a minimum—increases slowly with the thickness. For the thicknesses represented in the above table and figure this quasi-polarising angle has the values 58°, 60°, 62°, 63°, and 64°.

The azimuth (ω) is given in the following table:—

e_1/λ =	0·01.		0·02.		0·05.		0·1.		0·2.	
°	°	′	°	′	°	′	°	′	°	′
30	38	31	39	7	42	14	43	37	44	3
40	32	59	34	53	40	22	42	52	43	22
50	25	42	30	8	37	43	41	0	41	50
60	21	2	25	40	33	52	37	50	38	16
70	24	36	26	17	34	11	37	48	37	56
80	33	49	34	15	37	58	38	1	38	58

Fig. 22 below represents these values.

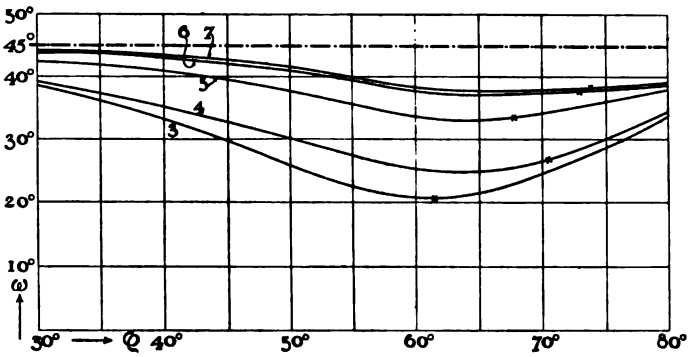


FIG. 22.

The crosses indicate the position of the Principal Azimuth, which increases through the following values: 21°, 26° 45′, 33° 30′, 37°, 37° 30′.

Finally, the phase difference (Δ) has these values:—

	0·01.	0·02.	0·05.	0·1.	0·2.
°					
30	0·008	0·033	0·046	0·055	0·058
40	0·028	0·086	0·105	0·104	0·105
50	0·079	0·190	0·214	0·190	0·178
60	0·483	0·317	0·335	0·280	0·273
70	0·887	0·493	0·525	0·440	0·428
80	0·990	0·755	0·805	0·695	0·665

These results are represented in fig. 23 below.

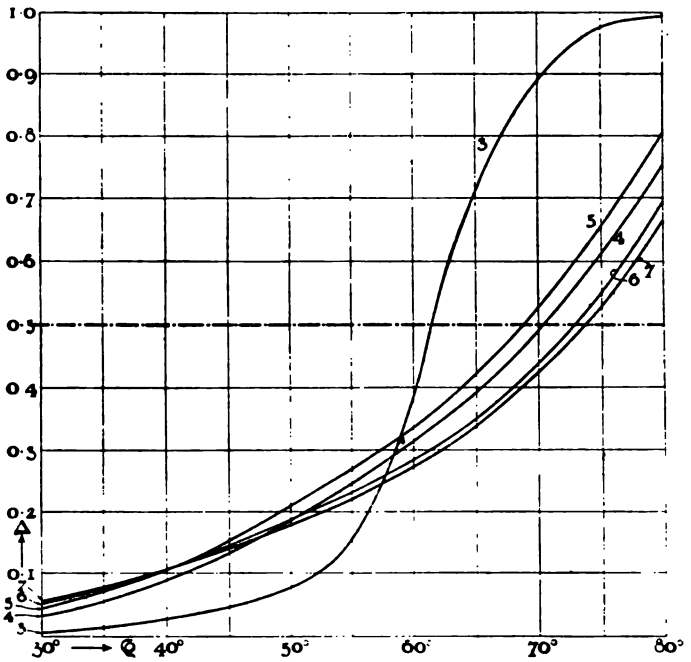


Fig. 23.

A comparison with fig. 17 above will show that the glass modifies the results in a very marked manner where the thickness of the metal is small. The difference of phase increases with the thickness for angles of incidence less than 40°. For larger angles, however, the law is completely different. When ϕ is greater than 60° the difference of phase at first diminishes rapidly with the thickness, then increases for a while, and afterwards diminishes again till it reaches the value appropriate to a thick plate. The Curve (3) corresponding to $e_1/\lambda=0{\cdot}01$ has a point of inflexion and cuts all the other curves. As is to be expected, its form is very similar to that of the curve representing the difference of phase in the case of reflection from glass or any other transparent medium when account is taken of the layer of transition.* The Principal Incidence, instead of increasing steadily with the thickness, as is the case with gold alone, increases rapidly at first, diminishes for a time and then increases again. Its values for the thicknesses here discussed are 61° 30′, 70° 30′, 67° 45′, 73° and 74°.

The graphical representation of Meslin's results in fig. 24 below will facilitate a comparison between theory and experiment.

* See 'Roy. Soc. Proc.,' 1905, p. 64.

On comparing this with fig. 23 above we see that the agreement is a close one. Curves *a*, *b*, and *c* of fig. 24 correspond to the following thicknesses as found by Meslin, 6 $\mu\mu$, 29 $\mu\mu$, and 41 $\mu\mu$; while *d* corresponds to Meslin's values for a thick plate. The Curve *d* is practically identical with the

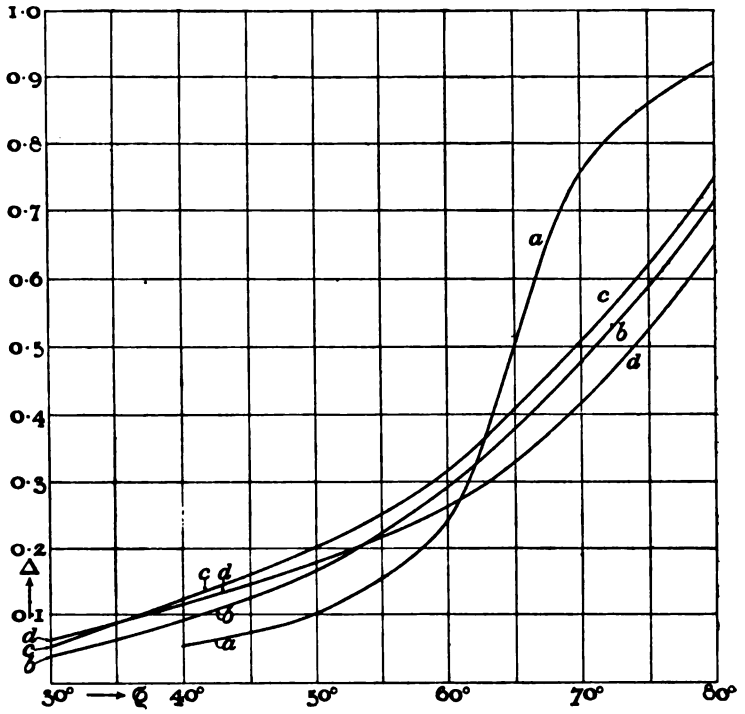


FIG. 24.

Curve 7 of fig. 23, while the Curves *c*, *b*, and *a* are very similar to Curves 5, 4, and 3 respectively. Taking $\lambda=760\,\mu\mu$, the thickness of the metallic film corresponding to the Curves *a*, *b*, and *c* is $0{\cdot}008\,\lambda$, $0{\cdot}038\,\lambda$, and $0{\cdot}054\,\lambda$ respectively. Comparing these numbers with the values of ϵ_1, corresponding to the Curves 3, 4, and 5, we see that the thickness of the layer of transition is of the order assigned to it on p. 330 above.*

* The surface conditions of the various films and of the thick plate were probably different, so that the layer of transition would not be the same in each. These results, however, indicate that the thickness of the layer was of the same order in each case. The uncertainty as to the refractive index of the glass has most influence on the thinnest film.

Experimental Evidence of Ionic Migration in the Natural Diffusion of Acids and of Salts.—Phenomena in the Diffusion of Electrolytes.

By Reginald Graham Durrant, M.A., F.C.S.

(Communicated by W. A. Shenstone, F.R.S. Received May 2,—Read June 21, 1906.)

1. The origin of the following experiments was due to observations made in jelly tubes with red phenolphthalein, prepared according to the directions given in Dr. Lüpke's "Elements of Electro-Chemistry,"* being a modification of Sir Oliver Lodge's original method.

After tracing, for some time, the bleaching progress from opposite ends of the tube, under the electro-motive influence of eight storage cells, the current was stopped and the subsequent bleaching progress was observed from either end.

The ends of the tube dipped respectively into hydrochloric acid and cupric chloride solution, and assuming the original bleaching to be due to hydrogen and to chlorine ions, it appeared probable that the subsequent bleaching was due to the same cause.

The mean relative rates of the ions under electro-motive stress of the battery were—

$$H : Cl :: 5{\cdot}7 : 1,$$

and the mean relative rates when the current was stopped—

$$H : Cl :: 5{\cdot}1 : 1.$$

The actual rates, in the second case, were naturally much slower and closely followed Stefan's law for diffusion, viz., distance covered varies as $\sqrt{\text{time}}$.

2. It occurred to the author that it should be possible to trace an advance motion of hydrogen ions in ordinary diffusion of acids into jellies, if the jellies were suitably prepared as indicators, and thus to illustrate, and perhaps to extend, the theory originally propounded by W. Nernst† and M. Planck.‡

3. Experiments on the Diffusion of Acids into Jellies.

As several hundred observations were recorded with various acids into variously prepared jellies, these observations are given as an appendix.

* English translation, p. 53.

† 'Zeits. für physikal. Chemie,' 1888, vol. 2, p. 613.

‡ 'Wied. Ann.,' 1890, vol. 40, p. 561.

The nature of the experiments and their more important results were as follows (1904):—

(*a*) By allowing acids to diffuse into jellies, suitably prepared and tinted with litmus, certain zones appear and become wider as time goes on.

(*b*) The foremost zone is in advance of the "diffusion front," and is well seen in a blue jelly having the following composition, calculated as grammes per cubic centimetre:—

Gelatine, 0·058; $KHCO_3$, 0·00128; KOH, 0·0002; Litmus, 0·0008;
or „ 0·06; „ 0·0006; „ 0·0002; „ 0·00084.

The gelatine was Coignet's "Gold Medal," and the "litmus" was simply the ordinary blue extract, twice filtered, and its weight found by evaporating a sample at 100° C. in a platinum dish.

This zone (*ad* in the tables) is purple. It starts from the diffusion front and fades away into blue higher up the tube. Its growth can be traced approximately (under good conditions) until it is 30 mm. long.

(*c*) The next zone (*ac* in the tables) is separated from the last by the diffusion front only. It is observable in the same jellies, and also in jellies containing more potash.

This zone is pale yellowish red, and at first is sharply marked at each boundary. It widens less rapidly than does the purple zone. Its back boundary, after about a week, becomes less clearly defined.

(*d*) After about 400 hours a third zone appeared in five cases, well behind the yellowish red and separated from it by red litmus. Like the purple zone, this was clearly defined at its back boundary and merged into red at its front.

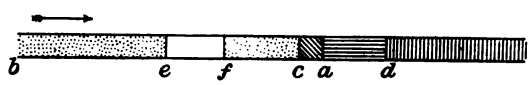


Fig. 1.

This zone becomes absolutely colourless. Its growth was noted from 426 to 760 hours in the cases of N/6·51 HCl, and N/6·51 HBr (p. 370). Also from 623 to 961 hours in the cases of N/5 HCl, N/5 H_2SO_4 and N/2 H_2SO_4 (p. 378).

The cause of this zone was not understood at the time, but the more recent results with silver nitrate, and also with calcium chloride (to be given later), show that it was probably due to the action of accumulating anions (Cl, Br, and SO_4) which had their origin at the concentration difference surface; in these cases, therefore, the origin was the bottom of the jelly tube dipping into the acid.

As a general result of the other observations it may here be noted—

(i) The foremost purple zone (*ad*) was obtained with hydrochloric, hydrobromic, sulphuric, nitric, and formic acids.

(ii) The contiguous yellow-red zone (*ac*) was obtained with HCl, HBr, H_2SO_4, and HNO_3, but not with formic acid; neither could it be obtained with oxalic nor with acetic acid, though these three acids were subject to exactly the same circumstances as were the first four.

The anions of HCl, HBr, H_2SO_4, and HNO_3 are, on reacting, all of them bleaching agents, while the other three anions, CHO_2, C_2O_4, and $C_2H_3O_2$, are not.

The author therefore believes that this yellow-red zone is due to these "bleaching" anions which are left behind when hydrions separate from the advancing diffusion front. The hydrions themselves, on reacting, produce the purple zone.

(The yellow-red zone never becomes bleached completely, because the action is constantly occurring in fresh litmus.)

4. Experiments on the Diffusion of Acids into Ferric Solutions without the Use of Jellies.

The earlier experiments with ferric solutions were made in the following simple apparatus:—

A tube (*ab* in figure) was fitted to a tap by means of an indiarubber joint. The ferric solution was drawn up short of this joint, and the lower (contracted) end was dipped into the acid as shown, the whole being surrounded by cold water and left for about 20 hours in a room where there was but little change of temperature. The tube was about 30 cm. long, and contained just over 5 c.c.

After 20 or 24 hours the tube *ab* was taken out and its contents run out, usually in six portions, into shallow porcelain cups, and there tested with potassium ferricyanide. At the same time blind experiments were made with other portions of the original ferric solution which had not been subjected to diffusion from the acid, and also with other portions which had been mixed with the same acid during the period of diffusion. The upper portions of the ferric solution indicated distinct reduction by giving a blue tint. The following experiments were made:—

Four experiments with normal sulphuric acid into a dilute ferric chloride solution.

Three experiments with stronger sulphuric into the same solution.

Two experiments with this stronger sulphuric into iron alum solution. All these showed considerable reduction.

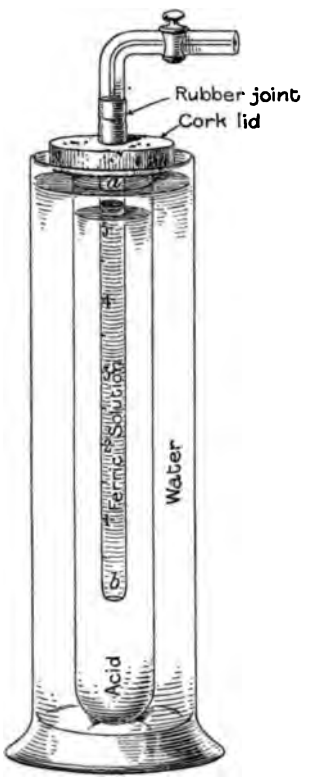


FIG. 2.

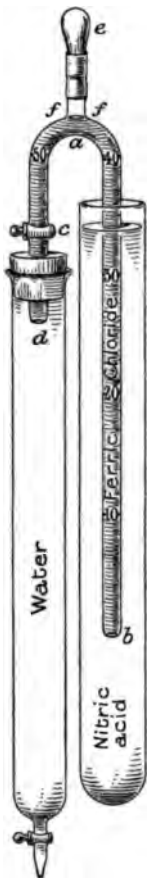


FIG. 3.

It was found, however, that a slow reduction does take place in all cases where sulphuric acid is used or where iron alum is used with other acids, though the difference in tint showed that greater reduction occurred after diffusion.

Preliminary experiments showed that no reduction occurs when ferric chloride solution is left mixed with hydrochloric acid; whereas in three experiments with 6N hydrochloric acid diffusing into ferric chloride (7·8 grammes per litre), distinct evidence of reduction occurred, as also in an experiment with 4N HCl into the same ferric chloride, and, later still, normal hydrochloric acid into a solution of ferric chloride, containing 1·4 grammes of iron per litre, gave two unmistakable cases where reduction had reached the top of the tube.

Only two experiments gave negative results, and in these the ferric chloride was taken from a bottle in the laboratory which had, for a long time, been in contact with air.

In order to make sure of observing this reduction, the ferric chloride (hydrated solid) should be dissolved in distilled water which has been previously well boiled. The potassium ferricyanide also should be free from dissolved air; in the later experiments (with hydrochloric acid and with nitric acid) the ferricyanide was delivered from a fine nozzle, and one drop only (= 0·015 c.c.) was used in each experiment.

In order to experiment with oxidising acids, another form of tube (fig. 3) was employed consisting of a syphon whose longer limb, *ab*, dipped into the oxidising acid, while the shorter limb, *acd* (with a ground glass tap at *c*), was connected with a burette.

A glass plug *e* fitting an indiarubber tube made it easy to regulate the exact level of the ferric chloride solution as indicated in diagram by *ff*.

This syphon (over 40 cm. long) held 9 c.c. from *a* to *b*, 2 c.c. *a* to *c*, and 1·8 c.c. *c* to *d*. It was filled completely with the ferric chloride, and the burette completely with water.

ab was then placed in a tube containing chromic or nitric acid, *c* was opened, and the burette tap very carefully turned so as to draw the acid up to about 30 mm. in *ab*.

After 20 hours or so the acid in its tube was removed; *e* was opened, which left the portion *ac* undisturbed. The branch *ab* was repeatedly rinsed with distilled water and the contents of the portion *ac* were tested. Distinct reduction was found in every experiment, two with chromic acid and three with nitric acid; in the two last experiments the nitric acid was 2·7N and the ferric chloride 2·24 grammes of iron per litre.

In all these experiments with acids diffusing into ferric chloride solution there is, therefore, evidence that hydrogen ions advance and cause some reduction of iron from the ferric to the ferrous state.

(There appeared also to be some evidence of an independent reduction on a smaller scale occurring at the free surface of the ferric chloride solution. Further experiments on this subject are contemplated.)

5. Three independent investigations have been attempted which bear on the results cited already. They were :—

(i) A set of experiments on the nature of the hydrogen occluded by palladium. These will be extended; the results up to the present seem to show that this hydrogen on leaving the palladium in purple litmus or red phenolphthalein is accompanied by hydrions sufficient to show acidity, amounting, however, to not more than 3×10^{-7} gramme of "acid hydrogen" available from the palladium helix employed.

(ii) An investigation to ascertain the best conditions for manipulating the ferricyanide reaction and to determine the maximum delicacy of the test.

(iii) An investigation of the sensitiveness of the litmus reaction—as compared with the ferricyanide reaction—since on these two reactions the evidence of hydrions advancing in front of diffusion hitherto depends.

(ii) *The Ferricyanide Reaction.*

The preliminary results of this investigation went to show—

(*a*) The blue or bluish green tint actually observed is due to the reaction

$$K_3Fe'''(CN)_6 + Fe''Cl_2 = 2KCl + KFe''Fe'''(CN)_6.$$
"Soluble blue."

(*b*) The reaction when observed on a surface of porcelain exposed to the air is more delicate in presence of large excess of ferric solution than it is when little or no ferric solution is present. This result is probably due to the excess of ferric iron obstructing the oxidation of ferrous iron by the air.

(*c*) The rapidity of the reaction is greatly increased by admixture of hydrochloric acid, a result analogous to that of acceleration in hydrolysis.

The method of experimenting, in the final work, was as follows :—

Rather more than a litre of normal hydrochloric acid was kept simmering for an hour and a-half, while pure hydrogen gas was bubbling through. This was allowed to cool in the hydrogen atmosphere. Then 24·1 grammes of iron alum were dissolved in the acid, so that the solution became at once normal hydrochloric and N/10 ferric, counted as 0·0028 gramme of ferric iron per cubic centimetre.

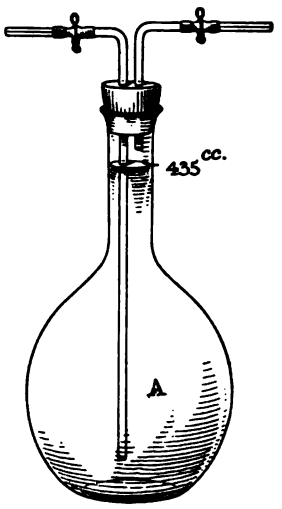


FIG. 4.

Two flasks had been prepared and fitted with short capillaries. Into the first, A (fig. 4), a portion of this solution was introduced till it was full to the 435 cubic centimetre mark, while another portion was introduced into the similarly fitted flask B (to a mark = 426 cubic centimetre). Hydrogen gas was bubbled through each to drive off air from above the mark. Into the flask A 0·0612 gramme of ferrous sulphate crystal was quickly dropped and was rapidly mixed and dissolved by passing more hydrogen through.

Both flasks were kept closed and, when used, the liquid was slowly forced out of the tube either by hydrogen or nitrogen gas. The flask A contained finally—

N.HCl (app.)
N/10 ferric iron
N/1000 ferrous iron

The flask B contained N.HCl and N/10 ferric iron.

Experiments with the two solutions dropped into phials with N/10 potassium ferricyanide at once showed very marked colour differences.

But as the test is usually made on porcelain, the volume of each drop as it fell from the capillary under nitrogen pressure was ascertained. This was 0·095 c.c. (practically 0·1 c.c.), and therefore each drop contained 0·0000028 gramme of ferrous iron from the flask A.

A tube with a fine nozzle was made to allow very small drops of the ferricyanide (N/10) solution to fall; each drop corresponded to 0·015 c.c.

Thus the volumetric ratios used in all the experiments were easily calculated with fairly good approximation.

In all the ratios of ferricyanide to ferrous iron (within very wide limits) the tints, as compared with the non-ferrous solution, were quite distinct, but the ratio which gave the most marked difference was when the ferricyanide added was ten times that required for the reaction

$$K_3Fe'''(CN)_6 + Fe''Cl_2 = 2KCl + KFe''Fe'''(CN)_6.$$

By mixing one drop from flask A with nine drops from flask B, and then adding the ferricyanide to portions of the mixture and comparing with the non-ferrous solution alone, a distinct green appeared in the former case. But when the ferricyanide was diluted to become N/100, and added to the now N/10,000 ferrous solution in the same volumetric ratio as was found best before, a very distinct green-blue colour resulted.

Thus, 0·00000028 gramme of ferrous iron, in presence of 1000 times its weight of ferric iron, and 10,000 times its equivalent weight of hydrochloric acid, appeared to show the "soluble blue" very clearly when 10 times its equivalent reacting weight of potassium ferricyanide was added.

(iii) *Sensitiveness of the Litmus Reaction.*

Approximately pure red litmus had been prepared early in 1905. Blue litmus solution, obtained by the action of water on the solid extract, was first mixed with considerable quantities of hydrochloric acid, and then was repeatedly dialysed through parchment paper into large quantities of distilled water, until long after all recognisable traces of chloride had disappeared. There was practically no passage of litmus through the parchment paper, but there was evidence of osmotic pressure at the parchment surface. The parchment was stained blue, possibly on account of a polarity change occurring within the material of the parchment.

The purest sample ("No. 4 dialysed litmus") had been largely used already in other experiments. It appeared to contain 59 times as much red litmus as mineral matter; this mineral matter consisted of colloidal ferric hydroxide and possibly aluminium hydroxide.

The sample "No. 3 dialysed litmus," which was used in the present case, contained—red litmus : mineral matter : : 17 : 1.

Ten cubic centimetres of this solution contained 0·0055 gramme of solid residue, of which 0·0003 gramme was left after ignition, consisting chiefly of Fe_2O_3.

A carefully prepared N/10,000 solution of potash (KOH) was titrated against this litmus solution. Five volumes of the potash against one volume of the litmus just gave the full blue coloration. The litmus solution was now made one-fifth strength, and then it was found that equal volumes of potash and of litmus produced the distinct blue.

It was easy, also, to perform the experiment on porcelain, as in the case of the ferricyanide reaction, and so to obtain strict comparison.

It appears that the litmus and the ferricyanide reactions are of the same order of sensitiveness, both giving obvious colour changes in N/10,000 solutions, even when less than a tenth of a cubic centimetre of the solution is placed on a white porcelain surface.

6. A Note on Certain Properties of Litmus.

Experiments with the "No. 4 dialysed litmus" showed—

(i) That it is an electrolyte (with an anion which, on reacting at the positive platinum electrode, became nearly colourless, as finally did the whole solution).

(ii) That this sample of red litmus will keep in a stoppered bottle for 16 months without apparent change and without any appreciable deposit.

(iii) That its rate of diffusion into water or jelly is exceedingly slow.

(iv) (already cited) That it dialyses very slowly indeed.

The experiment already cited with N/10,000 KOH and "No. 3 dialysed litmus" would suggest that the equivalent weight of red litmus acid is in the neighbourhood of 1000, but this would involve the assumption that equivalent reacting weights of litmus and of potash are those present, when the blue colour is reached, in these very dilute solutions, and this assumption is not necessarily correct.

However, the facts that litmus (i) *is* an electrolyte and (ii) appears to form a true solution are arguments against its being of a colloidal nature, and therefore (iii) the exceedingly slow diffusive rate is probably due, partly to its being a very "weak" acid, and partly to its possessing a very high molecular weight. ("Soluble blue," on the other hand, *is* colloidal. A solution, however dilute, will, on standing for a few days, deposit all colour.)

7. Experiments on the Diffusion of Concentrated Salt Solutions.

(i) *The Diffusion of Sodium Chloride Solution.*

It was found that a concentrated solution of pure sodium chloride, after boiling, became slightly alkaline.

To 10 c.c. of this solution five drops of a purple litmus solution were added and the mixture was placed at the bottom of a burette, the colour now being a light purple-blue.

To 20 c.c. of distilled water (previously well boiled) 10 drops of the same litmus solution were added, and by means of a platinum wire sufficient potash was also added to make the tint identical with that of the salt solution. The water litmus solution was carefully placed over the salt litmus solution in the burette, which was then corked.

After 23 hours a blue band was noticed just above the contact line, while the top portion of the water litmus became pinker.

In a similar burette a similar experiment was made, in which distilled water was placed above a salt solution which had been previously mixed with a few drops of phenolphthalein. The phenolphthalein was not reddened by the salt solution, but immediately the distilled water came in contact a pink layer appeared which developed into a band.

These experiments, which in themselves admit of more than one explanation, led to experiments with concentrated calcium chloride and with concentrated silver nitrate solution, the results of which appear to be of sufficient importance to justify a publication of results at this stage.

(ii) *The Diffusion of Concentrated Calcium Chloride Solution.*

Almost saturated calcium chloride solution occupied 14 mm. in a test-tube placed in a rather larger graduated cylinder surrounded also by water. Above it was placed a solution of purple litmus (the same as was used after dilution in most of the experiments to be described with silver nitrate).

After one day five or six long spiky crystals ($CaCl_2.6H_2O$?) formed at the bottom of the tube and were visible for three days (the corked bottle containing the stock solution of calcium chloride, placed close by, gave no crystals). Litmus gradually coagulated as a blue semi-solid deposit and covered these crystals, but left the supernatant solution colourless.

The diagram represents the state of affairs after seven days.

The band boundaries were very sharp indeed, and were accentuated (as was shown eventually) by a deposit on the glass.

If the top boundaries of these bands—viz., 41 mm. and 21 mm., are multiplied by 1·7, they become—

Top of bleached band ..... 69·7 mm.
„ blue band ..... 34·7 „

Bredig's values* for ionic mobilities, calculated for infinite dilution, are—

Chlorine..... 75·1 mm.
Calcium..... 33 „

The band boundaries were once more measured after nine days, and came out—

Top of bleached band ..... 48·5 mm.
„ blue band ..... 23·5 „

Multiply by 1·5—

Top of bleached band ..... 72·75 mm.
„ blue band ..... 33·25 „

On analysis, calcium chloride was found to have advanced beyond the bleached band. These results would imply that some accumulation of chlorine and of calcium ions had reacted (as shown) on the litmus.

On removing the solution carefully, no crystals were to be found beneath the deposit of blue litmus.

It would therefore seem that a temporary increase in concentration had occurred at the bottom of the tube, and, if so, this might be accounted for by supposing that the foremost layers of calcium chloride, on diffusing upwards, had, by mechanical reaction, forced back other molecules—the phenomenon being somewhat analogous to the evaporation of liquid carbon dioxide, whereby a freer and a less free state (the solid) are coincidently produced.

(iii) *The Diffusion of Silver Nitrate Solution.*

Crystals of silver nitrate were dissolved in a small quantity of distilled water, and two drops of a purple litmus solution were also added. This mixture was placed at the bottom of a 50 c.c. measuring tube, and altogether occupied 6·9 c.c. (fig. 6).

The tint was light pink, and the concentration was subsequently ascertained to have been 0·6689 gramme of $AgNO_3$ per cubic centimetre (nearly a 4N solution) (= 3·93N). Some of the same purple litmus was mixed with well boiled distilled water.

This was allowed to drop very slowly (sliding down the tube) on to the silver nitrate surface. A sharp blue line instantly appeared, which soon became convex upward. The total height reached up to the 30 c.c. mark.

The concentration of the litmus was calculated approximately by subse-

* Given on p. 95 of Lehfeldt's 'Electrochemistry,' (1904, Longmans).

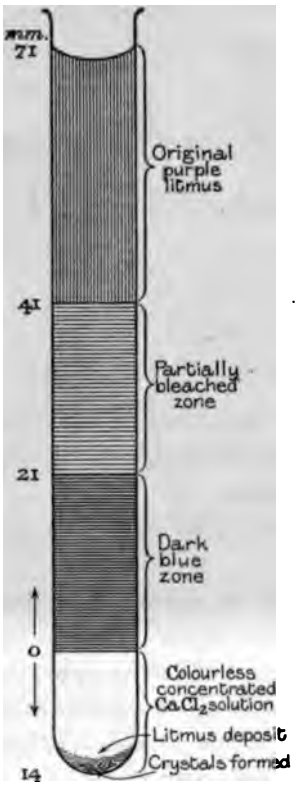


Fig. 5.

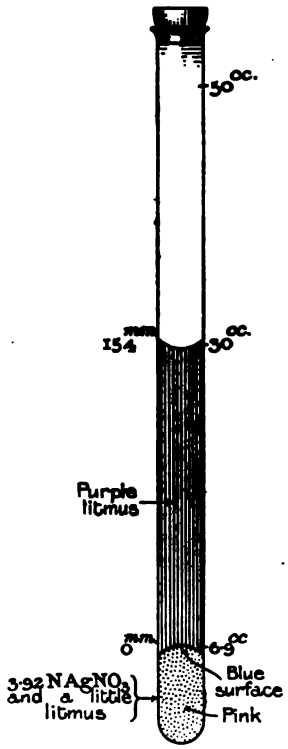


Fig. 6.

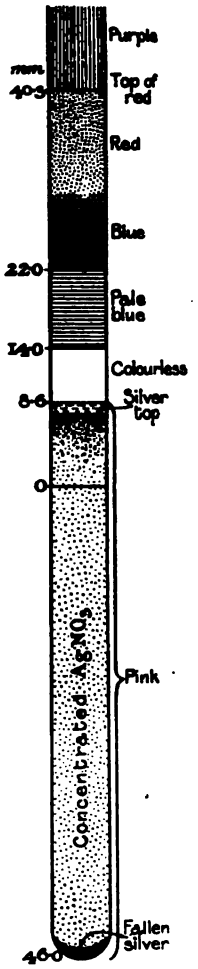


Fig. 7.

quent analysis from the contents of the bottle used. Expressed in grammes per cubic centimetre, it was roughly—

Alkali = 0·000007, calculated as OH.
Chloride = 0·000008, „ Cl.
Mineral matter ($Fe_2O_3Al_2O_3$, etc.) = 0·00006.
"Organic" matter, including litmus = 0·00009.

The tube was corked and surrounded by water in a cylinder. Careful observations were made at intervals from the start of 3, 28, 47, 77, 100, 123, and 143 hours. All the readings were taken from the division marks (in 0·25 c.c. intervals) of the containing tube; these readings were subsequently

translated into millimetre readings, starting from the original 6·9 c.c. mark. The number 6·9 was subtracted from each reading, and the difference number was then multiplied by 100/15, since 100 mm. happened to be the distance between 15-c.c. divisions.

One advantage of this enforced correction was to eliminate the influence of personal equation; moreover, each set of readings was made on a separate sheet of paper with no reference to, or recollection of, previous values.

The first observation was in itself of a somewhat startling nature, for after the first three hours three very sharply marked bands appeared—bright red, blue, and colourless—while immediately below the colourless band a deposit of silver was clinging to the glass, and more silver had dropped through the pink nitrate solution to the bottom of the tube.

The blue band, though sharply defined at each boundary (especially the lower boundary), was quite pale blue at its extremities, but near its centre a sharply marked deep blue band appeared. This deep blue zone persisted in the subsequent observations as the most striking feature in the general appearance.

On translating the readings into millimetres, as explained, it was found that the top of the red, the bottom of the deep blue, and the bottom of the colourless band were distant from the starting point (0 mm.) 40·3 mm., 22 mm., and 8·6 mm., while the top of the silver deposit was about 2 mm. behind.

The ionic velocities of hydrogen, hydroxyl, NO_3, and of silver at 1000 L dilution are from Kohlrausch's values—

H.	OH.	NO_3.	Ag.
285·8	154·3	58·3	49·9

The above millimetre readings if multiplied by seven become—

282·1	154	60·2

and although no reading was actually recorded of the position of the top of the silver deposit, a diagram was made at the time which would place it at about 2 mm. behind the 8·6 mark. This would give an approximate value of $6{\cdot}6 \times 7 = 46{\cdot}2$.

Subsequent observations made it clear that at first the silver deposit, after accumulating to a certain extent, dropped from the lower regions of its deposition on the glass, but that after the point 14 mm. had been reached, the silver (now less quickly forming) continued to adhere. Possibly by a coincidence this point, 14 mm., was (in the first reading) the point marking the top of the bleached band.

From the readings observed after the first three hours it appeared,

therefore, that four distinct bands were formed, and were due to reactions caused by ions of hydrogen, OH, NO_3, and silver, and that the top limits of the two positive tracks (H and Ag) and the bottom limits of the two negative tracks (OH and NO_3) were then in positions, when measured from the concentration-difference-surface, which were directly proportional to the relative velocity of these ions.

The results of the subsequent observations gave continuous curves for the four bands.

The chief points of interest are—

1. The rate of movement in the first three hours for all the bands was much greater than in former experiments.

2. A considerable concentration difference was maintained, since in the final examination of concentrations it was found that the last 7 c.c. had only fallen in strength from 0·6689 to 0·4352 gramme of silver nitrate per cubic centimetre.

3. The individual movement of the ions (as indicated by the bands) was probably due to high osmotic pressure in the silver nitrate, but a secondary influence may have been the attraction of congeries of H ions for OH and of NO_3 for Ag.

4. In the first observation (after three hours) the sharply marked bands were quite close to each other, and here this secondary influence must have been an important factor. It would appear that a set of sharply defined (though moving) fields of potential difference gave rise to the observation of those division lines which marked, almost exactly, the relative velocities of H, OH, NO_3, and Ag.*

5. In the later observations the red and blue bands were less sharply marked and were much further apart; both also were considerably removed from the source of energy.

The following calculations show that the tops of these two bands and also of the two others were, after 123 hours, at distances from the diffusion start approximately in the ratio of the square roots of the four ionic mobilities.

Calling the square root of the mobility of the silver ion = 100, the values (for 1000 L dilution) become—

* Subsequent experiments with silver nitrate showed evidence of discharges occurring at certain periods. In this case it is probable that discharges occurred at about the three-hour period.

	Ag.	NO_3.	OH.	H.
$\sqrt{\text{Mobility}}$	100	108·1	175·9	239·4
	mm.	mm.	mm.	mm.
Actual readings after 123 hours	Ag = 61·3 (top)	bleached band (top) 72·7	blue band (top) 94	red band (top) 136
Whence (× 100/61·3)	„ = 100	„ = 118·6	„ = 153·5	„ = 221·8

In other words, each "front" was approximating to Stefan's law for diffusion, each with its own constant.

6. Great care was taken in the final syphoning (performed with a special apparatus) and in estimating the silver present in the four portions selected.

Standard solutions of sodium chloride N/100 and N/10 were employed with chromate indicator. The last portion, 7·25 c.c. of still concentrated $AgNO_3$, was diluted 100-fold before estimation.

The results show that a very high fall in concentration occurred in the three portions taken from above the original silver nitrate solution. For whereas the mean concentration of this lowest portion was finally 0·4352 gramme $AgNO_3$ per cubic centimetre = *a*, that in the next portion (10·25 c.c.) was 0·1934 per cubic centimetre = *b*, that in the next portion (4·8 c.c.) was 0·00618 per cubic centimetre = *c*, that in the top portion (7·5 c.c.) was 0·00024 per cubic centimetre = *d*; or *b* was 1/2·25 of *a*, *c* was 1/31·45 of *b*, *d* was 1/25·66 of *c*.

These data are insufficient for a curve, but they indicate a geometrically progressive fall, so that the last few cubic centimetres at the top probably approximated to infinite dilution as regards $AgNO_3$. It is interesting to notice that silver nitrate was found in advance of the three lower bands.

(The late-forming bleached band, obtained in the diffusion of HCl, HBr, and H_2SO_4, similarly occurred well within the region which had previously become acid.)

Six further experiments on diffusion of silver nitrate into litmus have been made since this paper was originally communicated, and one parallel experiment was started on March 23—in which "No. 3" dialysed litmus was used—with the same silver nitrate solution.

In this parallel experiment the only apparent result after three hours was a slightly darker red band 2 mm. above the diffusion start, whereas with the common litmus, after three hours, the dark blue (bottom) was at 22 mm. and top of red was 40·6 mm.

Here after 19 hours the top of this band had risen to 5 mm.; the band

appeared now to be a more concentrated red than the red dialysed litmus above it. Referring to the curves for the original experiment, it appears that the top of the red should, at 19 hours, have been at 68 mm.

It would seem, therefore, that the effects, at any rate in this parallel experiment, were much less marked, and were about 13 times as slow as in the case where litmus containing small amounts of salts was employed. No silver deposit occurred.

The note made at the time was as follows:—"It therefore appears that diffusion will not appreciably occur when water practically free from ionisable matter is used, unless some action other than diffusion previously brings about the introduction of ionisable matter into the water."

I must at this point express my very great indebtedness to Professor Larmor, who, at an exceptionally busy time, not only made many valuable suggestions from the theoretical standpoint, but also examined the work of Planck and of H. Weber, which bears on the subject. In reference to the results of the parallel experiment just cited I quote from his memorandum the following:—

On the Theory of Ionic Migration in the Process of Natural Diffusion.

The following theoretical considerations must enter into the interpretation of results of experiments such as those described, of which a complete analysis would appear to be very complex:—

(i) Consider cases of diffusion starting from an initial state which involves no space measurements, *e.g.*, diffusion between long columns of salt solutions, ionised or not, which are separated initially at an abrupt plane surface.

The theory of physical dimensions requires that, as time goes on, corresponding lengths will vary proportionately to the square roots of the times which have elapsed since the beginning.

(ii) In all cases of natural diffusion it is a necessary condition that in each part of the volume positive and negative ions must be present in amounts electrically compensating, the very slight volume charge producing the potential gradient, which is involved on Nernst's theory in all cases of diffusion of electrolytes, being in this connection negligible.

This principle requires, as is known, that when only one electrolyte is present in solution in an absolutely non-ionisable solvent, its two ions must diffuse in company, whether we consider them to be dissociated or free; but when more than two ions are present they diffuse in virtual independence subject only to electric compensation everywhere in the aggregate.

(iii) If the liquid into which the ions diffuse is itself of sufficient conducting

power, we can consider each such wandering ion to be electrically compensated by an opposite charge accumulating round it as the result of electrolysis of this liquid, and all electric gradients as thus neutralised; it is only in such a case that each kind of ion present would diffuse at a rate determined by its own intrinsic mobility alone.

In a very dilute portion of the solution, or with slight diffusion-gradient, proportionately small conductivity of the solvent (such as the litmus solution *infra*) might suffice to realise this state of affairs.

(iv) When the conductivity of the upper liquid is slight, its ions diffuse down into the lower liquid, just as those of the latter diffuse up. Thus with impure litmus over $AgNO_3$ the H and OH ions travel rapidly down to meet the Ag and NO_3 which travel more slowly up; while with pure litmus there are only Ag and NO_3 and the colour effects travel much more slowly, in each case subject to the condition in (ii).

In the following experiments a fresh stock of silver nitrate crystals (triple crystallisation) was used. If a little concentrated solution of this was placed in red dialysed litmus or in purple-red ordinary litmus the solution became blue; but if a little purple litmus or just blue litmus was placed in the same concentrated silver nitrate solution it became red.

These results, probably depending on the ionisation of the litmus, made it difficult to say if the silver nitrate solution was really acidic, neutral or alkaline, but the results of all the diffusions (except the last, where nitric acid was mixed with $AgNO_3$) made it appear that the solution was not acidic, because the rates of band movement in their earlier stages were almost exactly half those of the March 23 experiment and H mobility : OH mobility :: 1 : 0·54.

In the first of these diffusions (April 30) 9·9 c.c. of 4·76 normal $AgNO_3$ diffused into a more concentrated solution of the same litmus as that used in the original experiment (March 23).

The diffusion was watched for 47 hours only and the curves made out as before.

At the end of three hours the following readings were made:—

	mm.
Centre of faint red (from start)	18
Top of blue band	11·3
Top of colourless band	4
No silver yet visible.	

Since the tops of the blue and the colourless bands were almost as the ionic mobilities of OH and NO_3, and as their rates were about half those

of the March 23 experiment, it was possible to calculate from the curves that the top of the red (though faint) should be at 19·7 mm.

Taking this value, the results come out thus—

	mm.	Ionic mobilities.
Top of red band	$19{\cdot}7 \times 14 = 275{\cdot}8$	$285{\cdot}8 = H$
Top of blue band	$11{\cdot}3 \times 14 = 158{\cdot}2$	$154{\cdot}3 = OH$
Top of colourless band	$4 \times 14 = 56$	$58{\cdot}3 = NO_3$

In the March 23 experiment all the readings after three hours were multiplied by 7 to give the Kohlrausch values.

The important difference to be noted is that here there was no sharp red band and that the above values were calculated for the tops of the bands, whereas, in the March 23 experiment, the top of red, bottom of deep blue, bottom of colourless, and top of silver deposit were proportional to the Kohlrausch values. In the present case there was no evidence of sharp discharge occurring at this time, nor in the subsequent observations. The faint red was probably due to hydrions coming down from the litmus above toward the upward moving hydroxyl. The further features were very similar to those which will be given in more interesting cases. Nine sets of readings were taken and the curves were very regular. The red, having reached a maximum intensity soon after three hours, became fainter and fainter. After 47 hours the top of blue and top of colourless band were at 57·3 mm. and 34·4 mm. respectively, the ratio being 1 : 0·600, while $\sqrt{\text{mobility OH}} : \sqrt{\text{mobility NO}_3} :: 1 : 0{\cdot}613$, a result which is in accordance with that in the later stages of the March 23 experiment.

An experiment with the same silver nitrate was started on May 2 into dilute "No. 3" dialysed litmus made blue by passing it through well washed moist silver oxide, Ag_2O; this blue colour, however, soon became grey and finally left a thin film all over the tube above the silver nitrate.

After 18·3 hours there was a fairly well marked yellow-brown band, the top of which was at 41 mm. and the bottom at 35 mm.

On referring to the curves of the last experiment (April 30), at 18·3 hours the top of red was at 42 mm. and the top of blue at 34 mm., *i.e.*, the centre in both cases was at 38 mm.

The conclusion drawn was that the top and bottom of this yellow-brown band corresponded to the top of red and top of blue in the previous experiment (the colour below was strongly brown).

The litmus in this experiment was much more dilute than in the previous experiment.

Without disturbing the tube, the upper liquid and some of the silver

nitrate was syphoned off slowly, and fresh 4·76N $AgNO_3$ added to reach the 10 c.c. mark. Then (May 3) very dilute litmus from the March 23 original bottle (1/50 strength) was added to reach the 40 c.c. mark on the tube, the whole being surrounded by water in a tall cylinder as before.

The concentration of this litmus (by analysis of 40 c.c. from the bottle) was :—

0·0058 OH (alkali)
0·0072 chloride (Cl)
0·048 mineral (Fe_2O_3, etc.)
0·085 organic matter, including litmus
} per litre.

The results of this experiment are represented in the accompanying chart and the only comments will be in reference to some of the letters given at the bottom :—

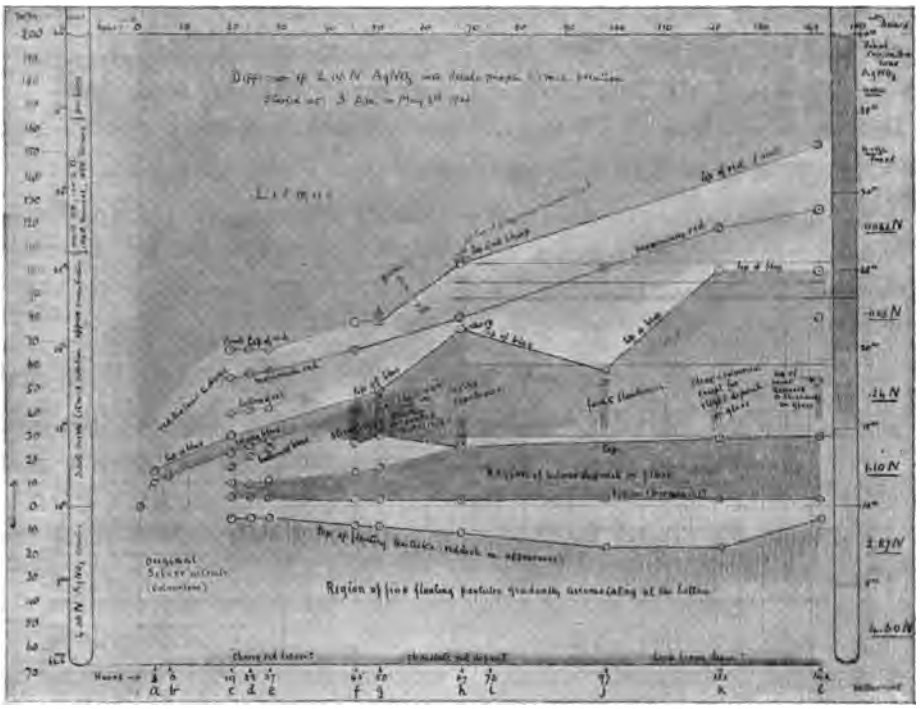


FIG. 8.

b Single observation of strong blue by gas light.

f Streamers begin to show from the strong blue. These streamers were observed in all the silver nitrate diffusions (except the last one to be given), but they began to appear at different periods. They consist of negatively

charged oxides of silver, Ag_2O and Ag_2O_2, and may also contain an insoluble silver salt of litmus at first.

g 50 hours (a critical period). The marks Δ represent very sharply marked surfaces, colourless between the two top surfaces, then sharp red, then, in the brown cloud, a very dark sharp boundary corresponding evidently to the bottom of the strong blue (blue colour now obscured by reaction with $AgNO_3$).

$$\frac{\text{Top of red}}{\text{Bottom of blue}} = \frac{78{\cdot}6 \text{ mm.}}{42{\cdot}6 \text{ mm.}} = 1{\cdot}845.$$

$$\frac{\text{Mobility of H}}{\text{Mobility of OH}} = \frac{285{\cdot}8 \text{ mm.}}{154{\cdot}3 \text{ mm.}} = 1{\cdot}852 \text{ (Kohlrausch).}$$

h (67 hours). Abnormal rise in the top of the blue-grey-brown cloud, thinner and extended rise of the granular silver deposit to meet the streamers which had descended.

Five sharply marked rifts in the film, due to the May 2 experiment already cited. These rifts were at—

102·6 mm., 95·3 mm., 88 mm., 60 mm., 30 mm. above 0 mm.
Differences 7·3 mm. 7·3 mm. 28 mm. 30 mm. 30 mm.

Note, $7{\cdot}3 \times 14 = 102{\cdot}2$ mm., top of red = top rift = 102·6 mm.

The first appearance of these now permanent rifts suggests that a discharge had occurred, before 67 hours, of sufficient intensity to set up vibrations (between the starting point and top of red) which broke the film. (The rifts were also measured by a colleague, Mr. J. A. Ensor, M.A.)

It would seem that a simultaneous discharge occurred between $\bar{H}$ and $\bar{OH}$ and between $\bar{NO_3}$ and $\dot{Ag}$, or, more strictly, between their products of reaction.

j (97 hours). Top of blue had fallen abnormally, cloudy portion above much clearer.

k (121 hours). Top of blue had again risen abnormally, all floating cloudiness had gone.

j and *k*. Change in tint of fallen particles below, and depression in the line of reddish floating particles.

Note also, on comparing position of maximum red in this experiment at 121 hours with that of March 23 at 123 hours, the values were—March 23 experiment 121 mm., this experiment 118 mm.

As a general inference it would seem that in this medium of very slow ordinary litmus solution the products of accumulated ions only discharge after a considerable lapse of time and that the discharge (judging from the abnormal movements following and from the rifts formed) is more acute than

it was after three hours in the first experiment (March 23), where the litmus was more concentrated.

The concentration curve for $AgNO_3$, obtained from analysis of eight portions, after 142 hours was very regular, showing a geometrical fall in concentration.

The next diffusion was made with the 4·76N $AgNO_3$ into litmus 1/40th instead of 1/50th of the bottle concentration. The results of this experiment (May 20) confirmed the inference just made.

No very sharp surfaces appeared and the line showing the top of the blue moved abnormally at the same periods, but in a less marked degree. After three hours—

$$\frac{\text{Top of red}}{\text{Top of blue}} = \frac{20 \text{ mm.}}{11{\cdot}3 \text{ mm.}} = 1{\cdot}77,$$

while

$$\frac{\text{H mobility}}{\text{OH mobility}} = \frac{285{\cdot}8 \text{ mm.}}{154{\cdot}3 \text{ mm.}} = 1{\cdot}852.$$

The most remarkable point of interest was the formation, after 24 hours, of a black bramble-like aggregation of crystals, exactly resembling those formed at the anode wire when silver nitrate solution is electrolysed in a porcelain dish (Ag_2O_2). The nucleus of these crystals was due to a minute drop of silver nitrate which touched the perfectly dry surface of the tube on removing the capillary pipette; the litmus was slowly allowed to trickle down, and, when the small drop was reached, a brown stream of Ag_2O detached itself from the glass and soon formed minute descending vortex rings; these stopped at a certain point and moved up as diffusion proceeded—till the above mentioned crystals formed and absorbed the brown deposit—and then continued to grow, ascending with the strong blue for the next 68 hours. At 101 hours from the start they were found broken into 16 fragments. These fragments continued to ascend as long as the observations lasted (up to 143 hours), but the fragments gradually moved apart, some rising well above the deep blue, and others, though still rising, actually taking up positions lower down in the blue.

This result was important because it proved the similar charge (no doubt negative) on the fragments causing mutual repulsion, while the actual rise of the cluster and finally of the fragments against gravity for 119 hours would point to a charge repelled upward by the negative NO_3 following, and at the same time attracted upward by, the positive H still higher up. It was possible in this case to trace the blue throughout the experiment, since these crystals took the place of the cloud in the former (May 3) experiment. Streamers appeared also at 100 hours and were observed at 117 and at 143 hours.

(Note.—The specific gravity of Ag_2O_2 is greater than that of very concentrated silver nitrate solution.)

Since the diffusion in all these cases where the triple crystallised silver nitrate was employed gave the earlier bands approximately with half the velocity of that observed on March 23, an experiment was started on May 23 in a smaller tube (25 c.c. graduations), when a little nitric acid was mixed with the $AgNO_3$ solution, 4·5N $AgNO_3$+0·019N HNO_3 being the concentration at the diffusion start.

The chart of these observations is given (fig. 10). The litmus was the same as that used in the last experiment. Here the nitric acid molecules were only 1/240 of the silver nitrate molecules.

At first (after five minutes) the red band, apparently shaped as in diagram (fig. 9), drew down blue from the purple litmus; this blue was soon removed by reaction with the red. Red only was apparent after one hour. After five hours an orange-red colour was seen below the top of the red. After 21½ hours the red had reached the top of the liquid in the tube. The approximately straight line from these observations shows that the top had only just been reached at 21½ hours.

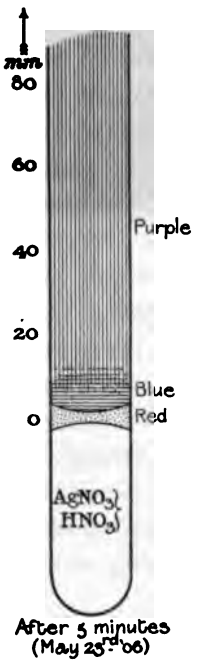


Fig. 9.

This distance (159·5 mm.) evidently traversed by the hydrions in this time was far greater than had been the case in any previous experiments, except those of the ferric chloride reductions.

Still more rapid colour transferences, however, had been obtained by silver nitrate diffusing into litmus containing considerable quantities of potassium nitrate, and there, as in this case, subsequent chemical action had been abnormally great. (The experiments with potassium-nitrate-litmus are not otherwise cited in this paper.)

The chart (p. 363) will explain most of the phenomena observed during 94 hours.

The hydrions, as shown in chart, would appear to descend from the free surface more rapidly than they went up and to influence the three other ions thus :—

(i) The hydroxyl, which showed by blue tint at the very top, on meeting with the continued stream of hydrions (from the original HNO_3) reacted to form water, so that the blue colour was gradually reduced to purple.

(ii) The NO_3, which showed (by bleaching) strongly at 30 hours and still sharply at 47½ hours, reacted with the hydrions to form HNO_3, *i.e.*, the ions (H and NO_3) again were brought into close proximity.

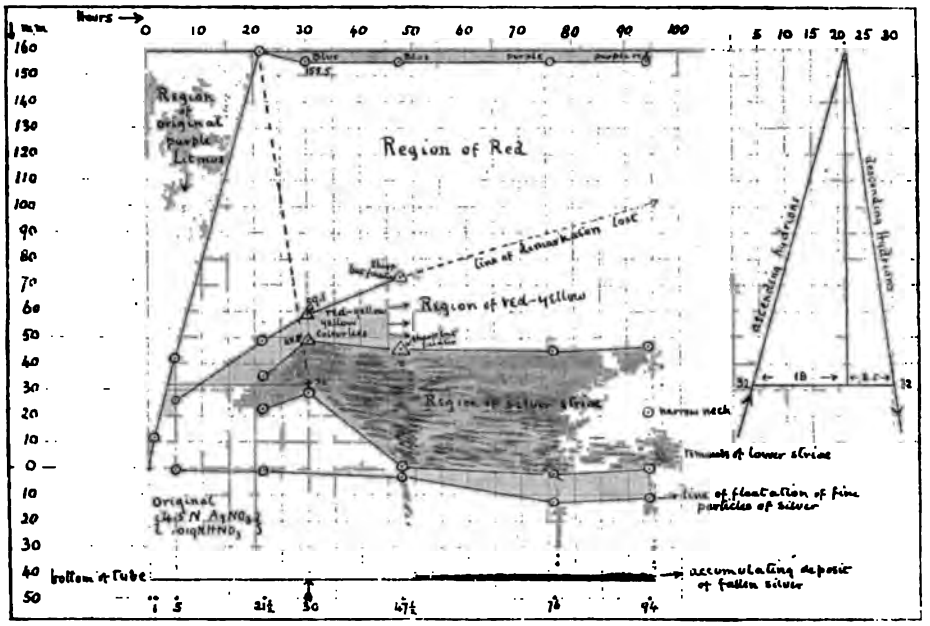

Hours →
Region of original purple Litmus
Region of Red
Region of red-yellow
Region of silver stria
Original 1·0 N AgNO3 + 0·01 N HNO3
bottom of tube
line of flotation of fine particles of silver
accumulating deposit of fallen silver

FIG. 10.—The critical period in this case was 30 hours.
Since blue (first appearance) was at 155·5 mm. to 159·5 mm.—

	mm.
Sharp top of yellow-red was at	59·1.
„ „ silver deposit was at	48·8.

The Kohlrausch values at 1000 L dilution give mobility of OH = 154·3
„ „ „ „ NO_3 = 58·3
„ „ „ „ Ag(ion) = 49·9

And since these three experimental values agreed closely with the Kohlrausch numbers, OH being now at the free surface, the position of the advance reflected hydrions would be, by calculation, within the silver region, near the mark 32 mm.

(iii) The positively charged silver particles, urged upward by the main diffusion and by following negative NO_3, were repelled downward by the returning stream of hydrions and the effect of horizontal striæ, resembling cirrus clouds, seen for the first time in these experiments, must have been due to these opposing forces from above and below.

General Remarks on Silver Nitrate Diffusion.

Concentrated silver nitrate solution gives results such as have been indicated above.

The phenomena differ largely according to whether the solution is slightly acid or slightly alkaline, also according to the concentration of the litmus solution and according to the concentration of electrolytes in that solution.

The chemical changes which occur when "acid acting" silver nitrate is allowed to diffuse appear to be as follows :—

(*a*) Advance hydrions ($\overset{+}{H}$) produce litmus acid (red).

(*b*) Hydroxyl ions ($\overset{-}{OH}$) manifest their effects, provided the hydrions are not in considerable excess.

Subsequent analyses show that silver nitrate advances with hydroxyl, and the blue colour gradually degrades through grey-blue to grey, on account of Ag_2O and, later, Ag_2O_2 being formed.

This deposit appeared to be negatively charged.

When nitric acid was mixed with silver nitrate in the molecular ratio $AgNO_3 : HNO_3 : : 240 : 1$, these hydroxyl reactions were not apparent.

(*c*) $\overset{-}{NO_3}$ ions, which follow $\overset{-}{OH}$, gradually bleach the blue litmus in front (when hydrions are in excess the red litmus is bleached); the oxidising action of these NO_3 ions may also account for the change of brown Ag_2O into darker Ag_2O_2 evident in the lower portions of the deposit.

(*d*) $\overset{+}{Ag}$ ions readily tend to assume the metallic form, as they are known to be endothermic.

It is probable (though not yet proved) that a silver-litmus salt is formed as long as litmus is in the neighbourhood of the deposit.

The first deposit at the bottom of the tube is cherry-red, then chocolate, then brown, and finally dark grey.

When "alkali acting" silver nitrate diffuses, the modifications in phenomena are as follows :—

(*a*) No advance red appears at first, that which appears later is induced by $\overset{-}{OH}$ drawing $\overset{+}{H}$ toward it from the purple litmus above.

(*b*) The early stage of band movement here is almost exactly half as rapid as it is with "acid acting" silver nitrate.

(*c*) The hydroxyl effects are much more marked—the deep blue degrades more rapidly to brown and finally to black (Ag_2O_2) unless, as was the case in one instance, the silver peroxide crystallises. The main deposit at the bottom is finally much darker.

Otherwise NO_3 bleaches as before and silver forms, partly settling as a granular deposit on the glass.

It is highly probable that this silver deposit is positively charged at first though the charge may be rapidly conducted away.

There is, therefore, strong evidence that H, OH, NO_3 and Ag ions accumulate in this order, while at certain critical periods (depending on the circumstances of concentration and admixture) these ions produce sharp

bands whose boundaries, when measured from the diffusion-start, are at distances almost exactly proportional to the known mobilities of the ions.

The author believes that the sharp bands are produced by a balance of forces—*viz.*, those due to osmotic pressure and accumulating charges. The phenomenon is somewhat analogous to the "flickering" which occurs when the actual velocity of a mixture of air and coal gas (due to pressure) is nearly equal to the explosion velocity, as has been demonstrated by Prof. Smithells.

In this case there is a "flickering" of ions over definite spaces, and therefore local chemical action evidenced by sharply marked effects.

In conclusion I would say that the experiment of May 23 and that of May 3 seem to have some bearing on the effects observed in atmospheric electrical discharge, the effects being slowed down here to a very great extent. I believe also that the general result, viz., the demonstration that ionic separation does appreciably take place in natural diffusion, will have some interest for the physiologist, because these conditions are fulfilled in the processes of diffusion in the body.

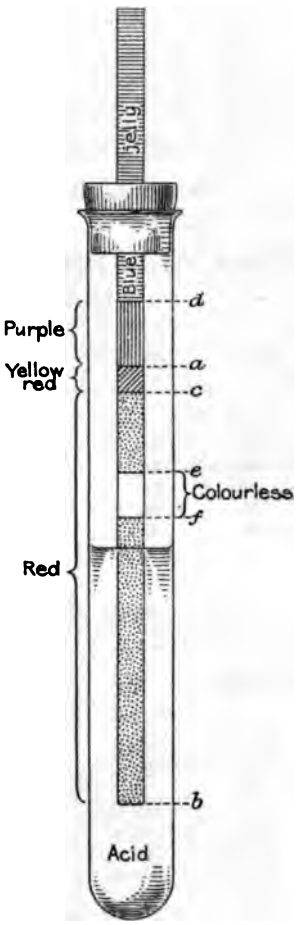


FIG. 11.

APPENDIX.

Observations on the Diffusion of Acids into Jellies Containing Litmus.

The general method employed is shown by the diagram (fig. 11).

The bands or zones *ad* and *ac* are those referred to in 3 (*b*) and 3 (*c*) on p. 343. The zone *ef* (3 (*d*) on p. 343) only forms after a long time and is considered on pp. 370 and 378.

Tubes of various cross sections were used, from 0·15 sq. cm. to 1·15 sq. cm. The cross section does not influence the rate of diffusion.

Tube A.—Jelly Purple with Litmus and $KHCO_3$. Tubes A, A′, and A″ placed simultaneously in Normal HCl.

Time.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	$bc/\sqrt{t}$.	*bc*/*ac*.
hours.	mm.	mm.	mm.	mm.			
25	40	36·3	3·7	10 app.	8·00	7·26	9·8
46	53	48·5	4·5	13 „	7·80	7·19	10·8
68	61	54·8	6·2	13 „	7·69	6·95	8·8
93	74	67·0	7·0	13 „	7·67	6·95	9·6
121	85	76·5	8·5	15 „	7·73	6·95	9·0
(Mean temp. 44° F. = 6·6° C.)				Average...	7·78	7·06	9·6

Tube A′.—Jelly Blue with Na_2CO_3 and Litmus.

Time.	*ab.*	*ac.*	$ab/\sqrt{t}$.
hours.			
46	54		
68	63	6	
93	75	6	
121	85		
320	149	—	8·3

Tube A″.—Yellow with Na_2CO_3 and Methyl Orange.

Time.	*ab.*	*ac.*	$ab/\sqrt{t}$.
hours.			
25	37		
46	54		
68	60	Very narrow.	
93	73		
121	83		
320	142		7·9

Tube C.—Same Jelly as in A, placed in N/3·7 HCl.

Time.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	$bc/\sqrt{t}$.	*bc*/*ac*.
hours.	mm.	mm.	mm.	mm.			
24	26·0	22·5	3·5	10 app.	5·31	4·59	6·43
70	45·0	38·5	6·5	12 „	5·49	4·62	5·92
137	63·0	54·0	9·0	14 „	5·38	4·60	6·00
191	74·0	64·0	10·0	17 „	5·36	4·63	6·40
213·5	78·0	67·5	10·5	18 „	5·34	4·59	6·43
235	83·0	72·0	11·0	20 „	5·42	4·69	6·54
262	86·5	75·0	11·5	21 „	5·34	4·63	6·52
(Mean temp. first 5 days 40° F. = 4·6° C.)				Average...	5·38	4·62	6·32

In Tube A diffusion constant for *ab* corrected for temp. at 2 per cent. rise per degree Centigrade gives 9·04 for mean temp. of 15° C.

Tube C similarly gives 6·48 for mean temp. of 15° C.

Note.—i. The diffusion constant* is here expressed as $ab/\sqrt{t}$, and in later experiments the value $bc/\sqrt{t}$ was not calculated.

ii. Experiments with sodium carbonate and with methyl orange jellies were not continued.

* This expression gives a constant which only holds for the given concentration; it follows from the equation $a = cq\sqrt{Kt/\pi}$, where a = quantity diffusing through area q, c = concentration difference.

An inspection of the foregoing tables shows—

(i) The diffusion marked by the growth of *ab* in Tube A was almost identical with the only diffusion observable in the Tubes A′ and A″. A sharply marked colourless strip, corresponding to *ac*, separated the boundary of pink coloration in the methyl orange Tube A″. This strip did not appreciably widen.

(ii) Comparing the Tube A with C—*i.e.*, normal HCl with N/3·7 HCl—it appears that the fall in the constant value $ab/\sqrt{t}$ (Stefan's law) from 7·78 to 5·38 was not accompanied by a corresponding narrowing of the yellow-red band *ac*, nor by any appreciable shortening of the purple-red region *ad*.

(iii) Comparing the Tube A with A″ it is evident that *a* marks the diffusion front, in other words, the band *ac* falls behind the boundary reached by the acid.

In the Tubes D and E next considered the same jelly was used.

The concentration of the acid diffusing was N/9 and N/27.

Tube D.—N/9 HCl.

Time.	*ab*.	*bc*.	*ac*.	*ad*.	$ab/\sqrt{t}$.	$bc/\sqrt{t}$.	*bc*/*ac*.	
hours.	mm.	mm.	mm.	mm. app.				
24	16	12·5	3·5	7·0	3·26	2·55	3·57	Jelly protruded and was cut off
52	24	20·0	4·0	12·0	3·33	2·77	5·00	}
76	29	24·0	5·0	14·0	3·32	2·75	4·80	}
100	34	28·5	5·5	15·5	3·40	2·85	5·18	}
116	36	30·5	5·5	17·0	3·34	2·83	5·54	}
				Mean...	3·35	2·80	5·12	

Tube E.—N/27 HCl.

Time.	*ab*.	*bc*.	*ac*.	*ad*.	$ab/\sqrt{t}$.	$bc/\sqrt{t}$.	*bc*/*ac*.	
hours.	mm.	mm.	mm.	mm. app.				
24	9	6·5	2·5	8·5	1·80	1·33	2·60	Jelly protruded and was cut off
52	13	10·0	3·0	9·0	1·80	1·38	3·33	}
76	17	13·5	3·5	10·0	1·95	1·55	3·85	}
100	20	16·0	4·0	15·0	2·00	1·60	4·00	}
116	21	17·0	4·0	15·0	1·95	1·57	4·25	}
				Mean...	1·95	1·52	3·86	

In comparing the results of the observations in the Tubes A, C, D, and E all with the same jelly—

(i) The band *ad* appears to be independent of the concentration.

(ii) The band *ac*, which was very similar in A and C, diminished in D and still more in E.

(iii) The ratio bc/ac became smaller as the concentration diminished, and appeared to rise steadily in E as time went on.

(iv) The values $ab/\sqrt{t}$ in the four concentrations became less as the concentration diminished, thus—

	In A.		In C.		In D.		In E.
Relative concentration	27	:	7·3	:	3	:	1
Relative value $ab/\sqrt{t}$	4	:	2·76	:	1·72	:	1

Since hydrobromic acid is known to diffuse at about the same rate as HCl, experiments were made to ascertain if these acids behave similarly as regards the formation of bands. In the first four tubes, the mixture used was gelatine, 10 grammes in 150 c.c., with a little caustic potash and not much litmus.

No bands were observed corresponding either to *ac* or *ad*.

These four tubes F, F, G, G, were placed respectively in N/2·17 HCl, N/2·17 HBr, N/6·51 HCl, N/6·51 HBr.

Tube F.—N/2·17 HCl.

Time.	Diffusion.	$ab/\sqrt{t}$ constant.
hours.	mm.	
18	32·0	7·51
42	49·5	7·64
74	65·0	7·56
116·5	81·0	7·50
144·5	89·0	7·41
	Mean	7·52

Tube F′.—N/2·17 HBr.

Time.	Diffusion.	Constant.
hours.	mm.	
18	31·5	7·42
42	49·0	7·50
74	63·5	7·38
116·5	80·0	7·41
144·5	88·0	7·33
	Mean	7·42

Tube G.—N/6·51 HCl.

Time.	Diffusion.	$ab/\sqrt{t}$ constant.
hours.	mm.	
18	23	5·40
42	37	5·71
74	47	5·46
116·5	59	5·46
144·5	67	5·58
	Mean	5·52

Tube G′.—N/6·51 HBr.

Time.	Diffusion.	Constant.
hours.	mm.	
18	23	5·40
42	37	5·71
74	47	5·46
116·5	59	5·46
144·5	67	5·58
	Mean	5·52

These results showed that the two acids behaved very similarly as regards diffusion at these concentrations.

In the next four tubes—H, H′, I, I′—the following mixture was used :—

Ten grammes gelatine, 130 c.c. water, 10 c.c. neutral litmus, 0·3 gramme $KHCO_3$, the whole kept below 70° C. and filtered.

The same acids and of the same strength were allowed to diffuse, using 25 c.c. of the acid in each case.

In no case did a band *ac* (yellow-red) appear until after 110 hours. Nine observations were made for each tube, extending over 426 hours.

The band *ad* (due to hydrogen) was seen at once, and grew regularly from 4 mm. to 26 mm. for the N/2·17 acids and from 5 mm. to 25 mm. for the acids of 1/3 of the concentration (N/6·51).

After 141 hours in each case a band *ac* was observed which, though it became more distinct as time went on, did not grow appreciably. It widened from 4 mm. to 5 mm. only with the N/2·17 acids and from 4 mm. to 6 mm. with the acids of 1/3 concentration.

The mean diffusion constants were—

N/2·17 HCl, 6·55,	N/2·17 HBr, 6·55,
N/6·51 HCl, 4·85,	N/6·51 HBr, 4·65,

whence the ratio of diffusive rates for the HCl N/2·17 to N/6·51 were 1·35 : 1, and for the HBr N/2·17 to N/6·51, 1·41 : 1.

Details of the tubes I and I′ are given on next page, and show the further formation of bands, which began to appear after 426 hours.

As the actual weight of litmus was not known in the H and I tubes, a third set of tubes, J, J′, K, K′, were filled with the following mixture, calculated for 1 c.c. of the jelly: Gelatine, 0·0666; $KHCO_3$, 0·00066; litmus, 0·0006. This solution was purple and did not show the band *ad*. The four tubes were watched for 159·5 hours, seven readings each.

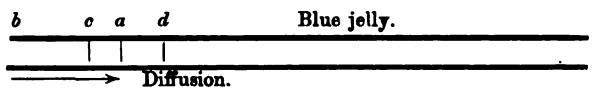
The band *ac* showed at once, increasing regularly. It was of the same dimensions for HCl and HBr throughout, and in the 1/3 concentration kept almost exactly 1 mm. wider than in the stronger acids.

Tables appended on p. 371.

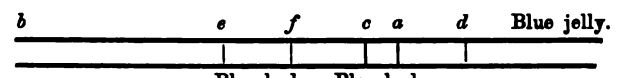
As the result of 76 readings of these 12 tubes in which the diffusion constants (*ab*) were taken—half for HCl and half for HBr—it seemed worth while to compare the results, allowing for differences of the mean temperatures during the periods of observation.

Comparative Diffusion with Tubes I and I′ containing same Jelly—100 c.c., 6·6 grammes, Gelatine, 0·2 gramme $KHCO_3$, and 6·6 c.c. Litmus as ordinarily made up.

I.—Diffusion of N/6·51 HCl.

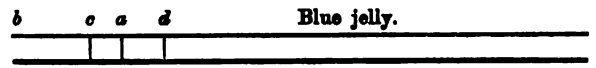


Time.	ab.	bc.	ac.	ad.	Diff. const. ab.	be.	bf.	ab/be.
hours.	mm.	mm.	mm.	mm. app.				
21·5	22	Not	—	5	4·03			
63·75	39	distinct	—	12	4·87			
92·25	47	enough to	—	15	4·80			
110	51	measure	—	15	4·87			
141	58	54·0	4·0	18	4·87			
166	62	58·0	4·0	20	4·81			
189	67	63·5	4·0	21	4·88			
				Average...	4·85			

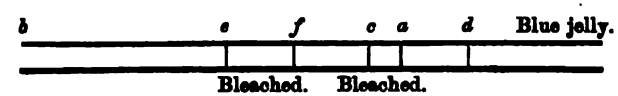


426	103	96·0	6·0	25	4·94	band *ef* noted sharp at *e*		
592	119	112·5	6·5	25	4·89	79	100	1·506
686	129	121·5	7·5	30	4·92	85	105	1·517
760	136	129·0	7·0	32	4·93	89	110	1·528
					4·92	Average...		1·517

I′.—Diffusion of N/6·51 HBr.



Time.	ab.	bc.	ac.	ad.	Diff. const. ab.	be.	bf.	ab/be.
hours.	mm.	mm.	mm.	mm. app.				
21·5	21·5	Not	—	5·0	3·97			
63·75	38·5	distinct	—	13·0	4·81			
92·25	45·0	enough to	—	15·0	4·68			
110	49·0	measure	—	16·0	4·68			
141	55·0	51·0	4·0	19·0	4·63			
166	60·0	55·5	4·5	20·0	4·66			
189	64·0	59·5	4·5	21·5	4·65			
				Average...	4·65			



426	98·0	92·5	5·5	25·0	4·74	band *ef* noted sharp at *e*.		
592	116·0	107·5	8·5	25·0	4·76	75	95	1·546
686	124·0	116·0	8·0	28·0	4·73	81	111	1·530
760	130·0	123·0	7·0	33·3	4·72	85	108	1·529
					Average... 4·74		Average...	1·535

J Tube.—N/2·17 HCl.

Time.	*ab.*	*bc.*	*ac.*	Diffusion constant *ab.*	*bc*/*ac.*
hours.					
16	26·5	23·0	3·5	6·62	6·57
23	32·5	28·5	4·0	6·77	7·12
39·5	43·5	38·0	4·5	6·92	8·44
46·5	47·0	42·0	5·0	6·89	8·40
71·5	58·5	52·5	6·0	6·92	8·75
95·5	68·0	61·0	7·0	6·96	8·71
159·5	89·0	80·0	9·0	7·06	8·88
			Mean ...	6·88	

J′ Tube.—N/2·17 HBr.

Time.	*ab.*	*bc.*	*ac.*	Diffusion constant *ab.*	*bc*/*ac.*
hours.					
16	27·0	23·0	4·0	6·75	5·75
23	32·5	28·5	4·0	6·77	7·12
39·5	42·5	37·5	5·0	6·76	7·50
46·5	46·5	41·5	5·0	6·82	8·30
71·5	58·5	52·0	6·5	6·92	8·00
95·5	68·0	61·0	7·0	6·96	8·71
159·5	88·0	79·0	9·0	7·00	8·77
			Mean ...	6·86	

K Tube.—N/6·51 HCl.

Time.	*ab.*	*bc.*	*ac.*	Diffusion constant *ab.*	*bc*/*ac.*
hours.					
16	20·5	16·0	4·5	5·12	3·55
23	24·0	18·5	5·5	5·00	3·36
39·5	32·5	27·0	5·5	5·01	4·91
46·5	35·5	29·5	6·0	5·20	4·91
71·5	43·0	36·0	7·0	5·09	5·14
95·5	51·0	43·0	8·0	5·22	5·37
159·5	66·0	56·0	10·0	5·23	5·60
			Mean ...	5·12	

K′ Tube.—N/6·51 HBr.

Time.	*ab.*	*bc.*	*ac.*	Diffusion constant *ab.*	*bc*/*ac.*
hours.					
16	20·0	15·5	4·5	5·00	3·44
23	24·0	18·5	5·5	5·00	3·36
39·5	32·5	27·0	5·5	5·01	4·91
46·5	35·5	29·5	6·0	5·20	4·91
71·5	43·5	36·0	7·5	5·15	4·80
95·5	50·0	42·0	8·0	5·12	5·25
159·5	65·0	55·0	10·0	5·16	5·50
			Mean ...	5·09	

The mean temperature for the first four days is given in each case.

	N/2·17 HCl.	N/2·17 HBr.	N/6·51 HCl.	N/6·51 HBr.	Mean temp.
	F 7·52 H 6·55 J 6·88	F′ 7·42 H′ 6·55 J′ 6·86	G 5·52 I 4·85 K 5·12	G′ 5·52 I′ 4·65 K′ 5·09	°F. 52·5 48·5 50·5
Mean diffusion constant for *ab*	6·98	6·94	5·16	5·09	50·5

It will be seen that the mean temperature for the J and K tubes happened to be the mean of the other two mean temperatures, and that the mean actual observation for the J and K tubes differs but slightly from the total mean readings for the three sets of tubes.

It would therefore appear that the diffusion constant for HBr is slightly less than for HCl.

Taking the mean readings (each representing 19 observations) and calling the diffusion rate of HCl = 100, the results are—

For N/2·17 acids ..... HCl = 100, HBr = 99·42.
„ N/6·51 „ ..... HCl = 100, HBr = 98·64.

It would also appear that the diffusion constant for HBr is reduced by dilution rather more than is the case with similarly diluted HCl.

Comparative diffusion experiments with normal HCl and normal H_2SO_4 into jelly composed of 10 grammes gelatine, 2 grammes $KHCO_3$, and 140 grammes water with neutral litmus :—

Tube O.—Normal HCl.

Time.	*ab.*	*ac.*	*ad.*	Diffusion constant.
hours.				
39·5	53	not well marked	6	8·44
67·75	70	„	9	8·50
90·0	82	7 about	12	8·65
118·5	94	6 „	15	8·64
		Mean ...		8·56

In the case of the HCl, after 90 hours 5 mm. jelly dissolved; after 118·5 hours 8 mm. jelly dissolved.

Tube P.—Normal H_2SO_4.

Time.	*ab.*	*ac.*	*ad.*	Diffusion constant.	Ratio HCl = 100.
hours.					
39·5	41·0	not well marked	6	6·53	77·3
67·75	55·0	5·0	10	6·68	78·6
90·0	64·0	6·0	13	6·75	78·0
118·5	72·5	6·0	15	6·66	77·1
160·5	85·0	6·5	16	6·71	
		Mean ...		6·66	77·8

Mean temp. 54·2° F.

It will be seen that the H_2SO_4 behaved in a similar way as regards formation of bands—the band *ac* being better marked than with HCl. This band, on the theory of ionisation, would be due to the ion SO_4 bleaching by oxidation.

In order to see if the band *ac* is only produced in cases where by theory an ion capable of bleaching is produced, the tubes J, J′, K, K′, were inverted and tested simultaneously with normal solutions of HCl, H_2SO_4, oxalic and acetic acids. Though these two last acids are believed to ionise slightly, their ions, C_2O_4 and $C_2H_3O_2$, would not be oxidisers.

In neither case did any band corresponding to *ac* appear. The observations give the relative diffusive rates.

The tubes were now called Q, R, S, and T (see p. 374).

In order to find the best proportions of ingredients for showing the bands *ac* and *ad*, several jellies were prepared—the ingredients were calculated as weight per 1 c.c.

	Gelatine.	$KHCO_3$.	KOH.	"Litmus" (from blue extract).
D.....	0·058	0·00128	0·0002	0·0008
E.....	0·06	0·0006	0·0002	0·00084
F.....	0·0664	0·00088	0·00026	0·00024
G.....	0·064	0·0014	0·0002	0·000175
H.....	0·0664	0·00066	0·0002	0·000182

Of these, D and E both gave very fair results, using N/2 HCl solution.

The results with these jellies were watched and recorded six times in 361 hours.

With D the band *ac* finally reached 7 mm. and *ad* 26 mm.
„ E „ „ 6 „ 25 „

and from comparative results it appeared that 0·1 gramme of $KHCO_3$ in 100 c.c. of jelly retards the diffusion constant for N/2 HCl by 4·5 per cent.

A further set of seven jellies was treated with N/4 HCl solution—the best was No. 7—(it showed *ad* very well) which contained in 1 c.c.—

Gelatine.	$KHCO_3$.	KOH.	Litmus.
0·05	0·0026	0·00023	0·0011

Four readings in each tube extending over 117 hours were made, from which it appeared that extra litmus did not appreciably retard the diffusion constant.

The addition of a small quantity of KOH makes the jelly sufficiently blue

Tube Q.—Normal HCl.

Time.	*ab.*	*bc.*	*ac.*	$ab/\sqrt{t}$.	bc/ac.
hours.					
28·5	47	43	4	8·80	10·7
49	60	55	5	8·57	11·0
80·5	77	70	7	8·57	10·0
121	94	86	8	8·55	10·7
			Mean ...	8·62	10·6

Tube R.—Normal Oxalic.

Time.	*ab.*	$ab/\sqrt{t}$.	HCl = 100.	Mean temp.
hours.				° F.
28·5	30·0	5·62	63·8	59·2
49	39·0	5·57	65·0	56·7
80·5	49·5	5·51	64·3	53·1
121	60·0	5·45	63·8	56·3
		Mean ...	5·54	64·2	56·3

These Tubes Q and R started at 11 A.M., May 29.

Tube S.—Normal H_2SO_4.

Time.	*ab.*	*bc.*	*ac.*	$ab/\sqrt{t}$.	bc/ac.	HCl = 100.
hours.						
24·5	33	30·0	3·0	6·66	10·0	76·8
46·5	46	41·5	4·5	6·74	9·2	78·6
76·5	59	53·0	6·0	6·75	8·8	78·7
116·5	71	64·0	7·0	6·57	9·1	76·8
			Mean ...	6·68	9·2	77·7

Tube T.—Normal Acetic.

Time.	*ab.*	$ab/\sqrt{t}$.	HCl = 100.	Mean temp.
hours.				° F.
24	28	5·71	66·0	59·2
46	40	5·90	68·8	56·7
76	51	5·85	68·2	53·1
116	58	5·38	62·9	56·3
		Mean ...	5·71	66·5	56·3

Tube S started 3.10 P.M., May 29.

Tube T started 3.40 P.M., May 29.

In Tube R an opalescence due to formation of calcium oxalate appeared; this cleared from the centre, the precipitate being carried toward *a* and *b* respectively.

In Tube T the limit mark *b* was not so sharply defined as in the other tubes.

The diffusive rate for H_2SO_4 compared to HCl 100 in these experiments gave value 77·7, with O and P Tubes 77·8.

to observe the band *ad*. From these experiments the retarding influence of the $KHCO_3$ (0·1 gramme in 100 c.c.) appeared to be only 2·1 per cent. on the diffusion constant for N/4 HCl.

Comparative Experiments on the Diffusion of certain Acids and of the Formation of the Bands *ac* and *ad*.

No. 1.—N/5 HCl.

ime.	*ab*.	*bc*.	*ac*.	*ad*.	$ab/\sqrt{t}$.	Relative diffusion rate HCl = 100.
ours.	mm.	mm.	mm.	mm. app.		
7·6	33·0	31·0	2·0	10·0	6·29	
1·25	45·0	42·5	2·5	13·5	6·28	
4	54·5	51·5	3·0	14·0	6·34	
6	67·0	62·5	4·5	16·5	6·22	
4·5	80·0	75·0	5·0	17·0	6·24	
2	91·0	84·0	7·0	19·0	6·25	
				Mean.....		100

No. 2.—N/5 HCl with 10 grammes NH_4Cl in 50 c.c.

Time.	*ab*.	*bc*.	*ac*.	*ad*.	$ab/\sqrt{t}$.	Relative diffusion rate.
hours.	mm.	mm.	mm.	mm. app.		
27·6	48	46·0	2·0	7	9·14	144·0
51·25	66	63·5	2·5	9	9·22	146·0
74	79	77·0	2·0	10	9·19	145·0
116	98	95·0	3·0	12	9·09	146·0
164·5	117	112·5	4·5	15	9·12	146·0
212	133	127·0	6·0	15	9·13	146·0
					Mean.....	145·6

No. 3.—N/5 H_2SO_4.

ime.	*ab*.	*bc*.	*ac*.	*ad*.	$ab/\sqrt{t}$.	Relative diffusion rate.
ours.	mm.	mm.	mm.	mm. app.		
7·6	27	25·0	2·0	10·0	5·14	81·0
1·25	37	34·5	2·5	14·0	5·16	82·2
4	44	41·5	2·5	14·0	5·12	80·7
6	55	51·0	4·0	16·5	5·11	82·1
4·5	66	61·0	5·0	18·0	5·15	82·5
2	74	68·5	5·5	22·0	5·08	81·3
					Mean.....	81·6

No. 4.—N/5 HNO_3.

Time.	*ab*.	*bc*.	*ac*.	*ad*.	$ab/\sqrt{t}$.	Relative diffusion rate.
hours.	mm.	mm.	mm.	mm. app.		
27	32·0	29·7	2·3	10	6·09	96·0
51	43·5	41·5	2·0	12	6·07	96·6
74	52·5	51·0	1·5	13	6·10	96·3
116	65·0	63·0	2·0	16	6·03	97·0
164·5	78·0	Line		21	6·08	97·5
212	88·0	indistinct		21	6·04	96·7
					Mean.....	96·7

No. 5.—Formic Acid.

Time.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	Relative diffusion rate.
hours.	mm.	mm.	mm.	mm. app.		
27	20·0	No band.		9	3·81	60·0
51	28·0			15	3·91	62·2
74	35·0			15	4·07	64·2
116	44·0			18	4·08	65·7
164·5	54·0			19	4·21	65·5
212	61·5			20	4·22	67·6
					Mean.....	64·5

No. 6.—N/2 H_2SO_4.

Time.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	Relative diffusion rate.
hours.	mm.	mm.	mm.	mm. app.		
27	32·5	30·5	2·0	8·0	6·19	97·5
51	44·5	42·0	2·5	12·0	6·21	98·1
74	58·5	50·0	3·5	12·5	6·22	98·2
116	66·5	62·0	4·5	14·5	6·17	98·2
164·5	79·0	73·5	5·5	17·0	6·16	98·7
212	90·0	84·0	6·0	17·0	6·18	98·9
					Mean.....	98·1

Composition of this jelly was in grammes per cubic centimetre :—

0·00125 "litmus," 0·00073 $KHCO_3$..... } a deep purple blue, called the "α" jelly.
0·06 gelatine (Coignet's), 0·000102 KOH }

It appears from these comparative experiments in "α" jelly—

(i) That the purple band *ad* was independent of the nature of the acid and of its concentration—indeed the readings for N/2 H_2SO_4 were less than for N/5 H_2SO_4.*

(ii) That the yellow-red band *ac* was apparent in all the acids except formic acid (whose ion, CHO_2, is non-bleaching).

(iii) That addition of ammonium chloride to N/5 HCl, to an extent equivalent to making it a 4 N solution as regards chloride, increased the diffusion rate in the ratio of nearly 3 : 2. Arrhenius has previously shown that with very concentrated ammonium chloride the rate may be increased as 2·24 : 1—and the result is believed to be due to the higher concentration of hydrions, $NH_4Cl = NH_3 + \overset{+}{H} + \overset{-}{Cl}$ occurring to a certain extent.†

(iv) Comparing the N/5 acids only, the relative diffusion rates come out—

HCl, 100, HNO_3, 96·7, H_2SO_4, 81·6, formic acid, 64·5.

* Although the band *ad* seemed rather shorter with N/2 than with N/5 H_2SO_4, the total distance *bd* was considerably greater, and again was almost identical with the distance *bd* for N/5 HCl.

† Voightländer's values at 20° C. are—

HCl, 100, HNO_3, 101·9, H_2SO_4, 58·9, formic acid, 42·1

('Zeits. für physikal. Chemie,' 1889. vol. 3, p. 316).

Table given in Whetham's 'Solution and Electrolysis,' p. 53, actual values—

HCl, 2·06, HNO_3, 2·10, H_2SO_4, 1·21, formic acid, 0·867.

The difference is due probably to the greater dilution in these N/5 solutions, which thereby become most nearly "isohydric."

(v) It would seem that an N/2 H_2SO_4 solution becomes, in the jelly tube, approximately "isohydric" with an N/5 HCl solution.

A seventh determination with N/2 H_2SO_4 was made, at the same time, in which the acid was placed in a wide tube above the jelly, the tube being corked. The object of this determination was to see if by any chance the purple band *ad*, hitherto assumed to be due to hydrions, was really due to CO_2 ascending.

The table here given is put side by side with that already shown (No. 6).

o. 6.—N/2 H_2SO_4 diffusion ascending.

ne.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	Relative diffusion.
rs.				app.		
27	32·5	30·5	2·0	8·0	6·19	97·5
51	44·5	42·0	2·5	12·0	6·21	98·8
74	53·5	50·0	3·5	12·5	6·22	98·2
16	66·5	62·0	4·5	14·5	6·17	99·2
64	79·0	73·5	5·5	17·0	6·16	98·7
12	90·0	84·0	6·0	17·0	6·18	98·9
				Mean.....		98·9

No. 7.—N/2 H_2SO_4 diffusion descending.

Time.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	Relative diffusion.
hrs.				app.		
27	33·0	31·0	2·0	9	6·29	100·0
51	45·0	42·5	2·5	14	6·28	100·0
74	53·5	51·5	3·0	14	6·22	98·2
116	67·0	62·5	4·5	15	6·22	100·0
164	80·0	74·5	5·5	18	6·24	100·0
212	90·0	83·5	6·5	18	6·18	98·9
				Mean.....		99·4

This result shows that the band *ad* forms equally well when the diffusion is descending. The diffusive rate appears to be slightly increased, but otherwise to be identical in its phenomena.

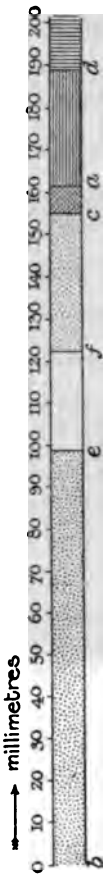
It is highly improbable, if carbonic acid gas is set free from the bicarbonate used in these experiments, that this gas would act to form the purple band equally whether it ascends or descends.

After a further interval these tubes with the "α" jelly were examined, and the late forming bleached band began to develop in the N/5 HCl, N/5 HCl + AmCl, N/5 H_2SO_4, and N/2 H_2SO_4—but not in the N/5 formic acid.

In the case of the N/5 HNO_3 the lower part of the jelly dissolved so that observations were impossible.

In the N/5 HCl + AmCl tube, though the band was observed after 623 hours, later on a gas was formed which forced the jelly out from the lower end of the tube.

The following were the measurements recorded (July 10—24, 1904):—



	Time.	*ab.*	*bc.*	*ac.*	*ad.*	$ab/\sqrt{t}$.	*be.*	*bf.*
				No. 1.—N/5 HCl.				
	hours.							
Hot weather	623	140·5	132·5	8·0	30	5·63	90	111 app.
	793	163·0	155·0	8·0	36	5·78	103	indistinct
	961	185·0	176·5	8·5	blocked	6·00	127	„
				No. 3.—N/5 H_2SO_4.				
Hot weather	623	115	107	8	28	4·61	90	joins *ac.*
	793	135	125	10	37	4·79	99	„
	961	152	140	12	45	4·90	104	„
				No. 6.—N/2 H_2SO_4.				
Hot weather	623	140	133·0	7·0	30	5·61	88	112 app.
	793	162	155·0	7·0	27	5·75	99	123 „
	961	185	176·5	8·5	blocked	6·00	114	indistinct

The diagram represents the diffusion of N/2 H_2SO_4 after 793 hours.

The chief interest attaching to these observations taken on the 26th, 33rd, and 40th day after the diffusion was started is—

(i) The N/2 H_2SO_4 continued to keep pace with the N/5 HCl.

(ii) The lower, sharply-marked boundary of the bleached band *c* made its first recorded appearance at points nearly identical in each case,—for N/5 HCl at 90 mm., for N/5 H_2SO_4 at 90 mm., for N/2 H_2SO_4 at 88 mm., from the bottom of the tube.

(iii) The progress of this point *e*, however, varied, and its position after the 40th day (961 hours) was for N/5 HCl at 127 mm., for N/5 H_2SO_4 at 104 mm., for N/2 H_2SO_4 at 114 mm., from the bottom of the tube.

If, as it has been already suggested, this late forming bleached band is due to the anions Cl and SO_4, then the rates of progress here observed are what would be expected, because SO_4 is known to have a lower mobility than Cl.

The table due to Kohlrausch and Holborn, and given on p. 102 in Lehfeldt's "Electro-Chemistry," shows that the relative molecular conductivities for HCl and H_2SO_4 at 200 L dilution (18° C.) are—

$$HCl : H_2SO_4 :: 1 : 1{\cdot}77,$$

or

$$HCl : \tfrac{1}{2}H_2SO_4 :: 1 : 0{\cdot}885.$$

The values for e on the 40th day for N/5 HCl and for N/2 H_2SO_4 were 127 mm. and 114 mm., or—

$$HCl : \tfrac{1}{2}H_2SO_4 :: 1 : 0{\cdot}898.$$

This comparison is made on the assumption that the N/5 HCl and the N/2 H_2SO_4 became, in the jelly tubes, practically isohydric, because their diffusion rates were equal. If this was the case, then the movement of the anions Cl and SO_4 in the dilute acid jelly would be equally affected by the movement of the hydrions also present, and thus the progress of the anions would be comparable.

A number of experiments (not all cited) were made with litmus jellies not containing salts other than those in the jelly and litmus employed.

In these experiments there was hardly any appearance of the bands *ad* and *ac*. This non-appearance would seem to be in keeping with the conclusions arrived at by Walker, McIntosh, and Archibald :—*

"The conclusion we feel justified in drawing from these observations is that in at least a great number of cases, if not in all, combination with the solvent is the necessary precursor of ionisation, although such combination does not necessitate ionisation."

Conclusions.

The results as given in the present paper would appear to afford a considerable body of data tending to support the theory of Nernst and Planck.

So far as the author is aware, the method of studying band boundaries has been almost entirely confined to experiments in which batteries have been employed, as in the work of Orme Masson and of Steele.

The earlier experiments in jellies and the later experiments with silver nitrate and calcium chloride show that very fairly sharp bands are obtainable without batteries.

The evidence goes to show that hydrogen ions move in advance of the diffusion front, whereas other ions produce their various "effects" in the rear of the diffusion front.

* "Ionisation and Chemical Combination in Liquid Halogen Hydrides and Hydrogen Sulphide," 'Chem. Soc. Journ.,' July, 1904, CXII, vol. 85, 4D, p. 1105.

The Action of Radium and certain other Salts on Gelatin.

By W. A. Douglas Rudge, M.A.

(Communicated by Professor J. J. Thomson, F.R.S. Received June 7,—Read June 21, 1906.)

[Plate 7.]

The action of radio-active substances on gelatin media has recently attracted attention. In 'Nature'* there appears a letter by J. B. Burke, in which the writer states that certain "bacterial-like" cells are obtained as the result of the action, the cells grow up to a certain stage and subdivide, they contain a nucleus, and appear to be highly organised bodies. The author has made numerous experiments on this subject, and has made several communications to 'Nature' and to the Cambridge Philosophical Society.

The present paper deals chiefly with the results obtained by the aid of photography, which obviously is a much more satisfactory method of recording than mere drawing.

The word "growth" is used to indicate the action, but must not be taken to imply that anything of the nature of living growth has occurred.

Two methods of working were employed: (1) for unaided eye observation; (2) for microscopic examination.

In the first method small Soyka flasks with parallel sides were employed to hold the gelatin culture medium. The flask was about half filled with the gelatin and sterilised in the usual way by steaming. A few specks of the radium salt were then placed on the surface of the gelatin and the effect watched. At once a whitish patch was seen to develop round the speck, the patch rapidly increasing in size, so that at the end of 10 minutes it appeared like a growth of ordinary mould.

Plate 7, fig. 1A, represents the appearance of the growth at the end of about an hour. The patch continued to grow, but at a much slower rate, and in some cases reached a maximum in less than a day, the time required depending upon the stiffness of the jelly and upon the class of gelatin used. Several samples of radium salts of different degrees of purity were used, and it was seen that the rate and amount of growth did not depend upon the amount of radium present in the sample. Solutions of the salts were sometimes used, but the solid material was more satisfactory; the general

* Vol. 72, p. 78.

result was, however, the same. As radium salts are composed in the main part of barium salts, it seemed likely that the latter might have some effect upon the gelatin, and this was found to be the case, a growth being produced which seemed identical with that produced by the radium salt (fig. 1B). Fig. 2 shows the extent to which the growth had penetrated after 36 hours, and after which it ceased to increase.

A systematic examination was next made with all kinds of metallic salt, with the result that only those of strontium and lead, besides radium and barium, gave any decided effect. As these metals are those which form insoluble sulphates, it seemed likely that the growth originated about the precipitates which form with the sulphur compounds present in the gelatin.

As the use of the gelatin in the culture material is simply for the purpose of localising the growth, by keeping it more or less fixed, the effect of using other glutinous or mucilaginous substances instead of gelatin was tried. The substances thus employed were agar-agar and several varieties of starch and gums, sufficient being added to the meat solution to cause it to solidify. When this was done it was found that if *distilled* water was used in making up the jelly, *no growth could be seen*, but if *tap* water was used a slight growth made its appearance, and if a soluble sulphate was previously added, then a *very dense* growth appeared. It thus was quite evident that the presence of a sulphate was necessary for the formation of the growth, and attention was then directed to the gelatin to ascertain whether sulphuric acid or a sulphate was usually present. Between 30 and 40 samples of gelatin were examined and, with three exceptions, all contained sufficient sulphuric acid to give a distinct, sometimes a dense, precipitate with barium chloride in presence of nitric acid.* The gelatin solutions were prepared by washing the sample six times with distilled water, allowing it to soak for some time before decanting, then dissolving in sufficient distilled water to make a thin jelly.

Two samples of commercial Russian isinglass and one sample of gelatin prepared by the author from fresh calf skin failed to give a precipitate with barium or radium salts, but in each of these cases a growth could be obtained by adding a soluble sulphate. If a barium salt gave no precipitate with the gelatin, then radium salt failed to produce a growth. It thus seemed clear that the growth originated about the precipitate of barium sulphate.

The growth continues to extend for some time into the gelatin, but after a while it stops. The reason for this extension of the growth from the point of contact appears to be as follows: the gelatin allows of a slow diffusion of the

* The precipitate was analysed in several cases, and was found to consist of $BaSO_4$.

barium salt through it, and as there is only a small amount of sulphuric acid present the barium is in excess and, therefore, after forming a precipitate in the first layers of the gelatin, sufficient barium salt is left, which, diffusing onwards, causes further precipitation in the succeeding layers, but eventually all the barium salt is used up by combining with the sulphuric acid and then the growth reaches its limit.

A proof of this theory is given by the fact that, with samples of gelatin containing a (relatively) small amount of sulphuric acid, the growth, although much less dense, extends for a greater distance.

Figs. 3 and 4 are photographs of two flasks containing very pure gelatin. To 3 there was added a small amount of calcium sulphate solution, to 4 twice the amount was added. The growth can be seen to extend much further into the gelatin in 3 than in 4, although it is much less dense. Many observations confirm this.

As the experiments conducted in the flask did not admit of the action being watched from the beginning, another method was adopted which allowed of continuous observations being made. This method consisted in placing a little of the melted jelly upon a glass slip and, after allowing it to solidify, adding a speck of the salt whose action was to be studied and then covering with a thin glass circle. A modification of this plan was to place the cover glass upon the still liquid gelatin and allow it to solidify under the cover. A speck of the salt was then placed at the edge of the cover glass, and the growth worked its way through the thin layer of gelatin enclosed between the glasses. Many hundreds of preparations were made in this way, using all kinds of salts, and the results obtained have been the same as in the flask experiments, viz., that radium, barium, strontium, and lead salts are the only ones which produce any effect. It might be expected that calcium salt should behave in the same way as barium and strontium, but the calcium sulphate is so much more soluble than the sulphates of the other two metals that it does not form a precipitate under the conditions of the experiments.

Very careful search was made in the case of uranium salts, but not any growth could be obtained, negative results also following the use of thorium salts, pitchblende, and uranium metal. There is thus no connection between radio-activity and the formation of the growth.

A number of photographs were taken of the preparation made by the latter method at periods from a few minutes after contact with the gelatin to several days and in some cases weeks.

The apparatus used for this purpose was supplied by Zeiss, and for direct observation magnifying powers up to 1500 diameters could be employed.

For photography and projection magnification up to 6000 or 7000 diameters could be obtained without undue distortion. Photographs were taken with magnifications of 400, 1000, and 4000.

The first effect of the action of radium salt was to cause an evolution of gas in the form of minute bubbles, owing to the decomposition of the water; the evolution soon ceased, but simultaneously a nebulous growth was seen to proceed from the point of contact of the salt with the gelatin. The growth consisted of tiny particles of precipitate which increased in size rapidly up to a certain point, and then expanded much more slowly, and in many cases did not increase at all after 10 hours. This precipitate has, undoubtedly, a sort of cellular structure, as is clearly shown in the photographs taken with the higher powers.

Figs. 4 to 8 show the progressive stages of the growth during 85 minutes, the magnification being 400 diameters. Many "pairs" of cells can here be seen, but the grouping is purely fortuitous.

Fig. 9 represents a portion of the same preparation taken with a magnification of 1200 diameters. Here the cellular character is clearly seen. This same preparation was used to see whether any increase of size took place after one day.

For this purpose the slide was fixed firmly to the stage of the microscope, and the objective, 1/12 oil immersion, focussed upon a large cell which had a well-defined shape. This was photographed at intervals of a day for four successive days in order to determine whether there was anything of the nature of "cell division" or growth, in the usual sense, taking place (figs. 10 to 13).

The photographs absolutely negative this idea. Observation could not be carried on for a longer time on account of the drying of the immersion oil. It is important to observe that there is no *trace of a nucleus*, even on pushing the magnifying power by projection up to 12,000!!, this figure being, of course, a long way past the limit of "useful" magnifications.

A series of photographs was taken with barium salts instead of radium, with the results shown in figs. 14 to 17.

Fig. 14 shows the nature of the growth after 15 minutes at 400 diameters, fig. 15 after 30 minutes, fig. 16 the appearance at 1200 after one hour, and fig. 17 at 4000. It appears that there is not much difference between the result of the radium and barium salts: in fact, it is often impossible to say which metal has caused a particular growth. There is a considerable variation in the effect of both radium and barium salts, owing to the varying nature of the different samples of gelatin, and to the amount of water present, etc.

Fig. 18 shows the result at 4000 diameters of the action of strontium nitrate, and fig. 19 that due to lead nitrate upon the gelatin.

If these experiments are conducted upon gelatin from which the sulphuric acid has been removed no growths are obtained. A sample of gelatin from which the sulphuric acid had been removed was sealed up with some radium salt in September last, and at the present time no signs of growth have made their appearance, but if to a portion of the gelatin a soluble sulphate is added a growth at once appears.

It thus seems to be quite clear that the cellular growth cannot be produced by radium or barium unless a sulphate is present, and other metals, save Sr and Pb, fail to produce any result, because they do not form insoluble sulphates.

The cellular form of these precipitates is probably due to the circumstance that the gelatin is liquefied by the actions of the salt, and each particle of precipitate is formed about a core of gelatin, so that the layer of barium sulphate forms a kind of sac or cell which is surrounded by the solutions of the salt in the liquefied gelatin. This *cell* may be permeable to the liquefied gelatin containing a salt in solution, which, passing through the cell wall, causes an expansion to take place, the limit of growth being controlled by some surface tension effect.

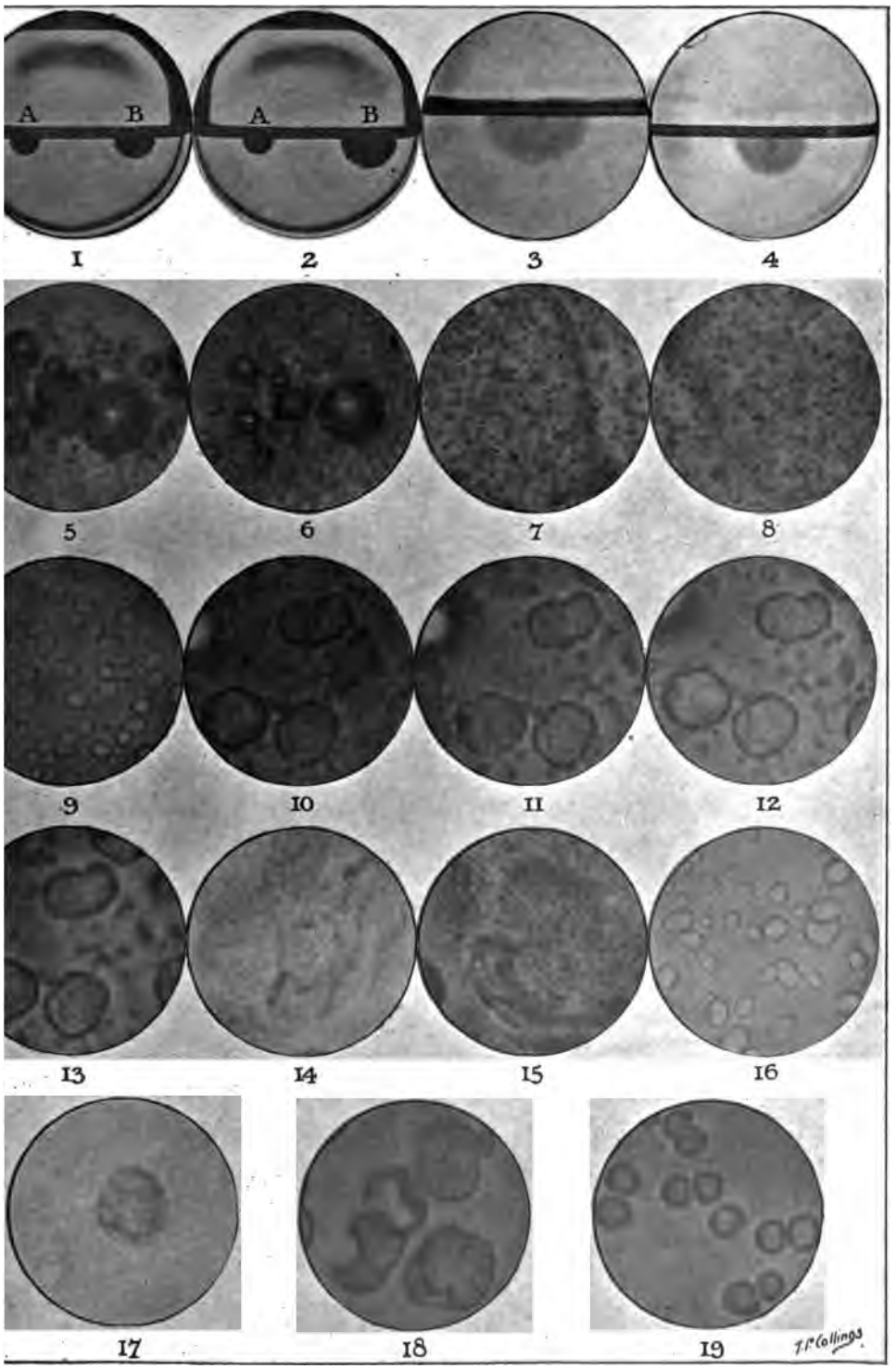
The conclusions which are drawn from a study of the photographs and direct examination under the microscope with high powers are that:—

1. The cells form round a precipitate of an insoluble sulphate, and the energy of the growth of the cell depends upon the amount of sulphate present.

2. *Radium has no specific action in forming cells*, any effect produced being due to the barium associated with it, and the purer specimens of radium salts are less satisfactory as cell-formers than the impurer ones. Probably pure radium salt would have no action except that of causing an evolution of gas.

3. The cells do not divide or bud or show anything resembling "karyokinesis," their growth very quickly reaches a maximum, and they do not decay or split up, save as a consequence of the drying of the gelatin. If the cover glass is sealed down with cement, the cells have been observed to suffer no alteration in the course of four months.

4. Radio-active substances, unless they contain barium, do not give rise to the formation of cells.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The Composition of Thorianite, and the Relative Radio-activity of its Constituents.

By E. H. BÜCHNER, Ph.D.

(Communicated by Sir William Ramsay, F.R.S. Received August 23,—Read November 8, 1906.)

[*Prefatory Note by Sir William Ramsay.*—When the cubical mineral from Ceylon, sent to me by Mr. Holland in December, 1903, and named by Professor Dunstan "Thorianite," was analysed by several of my students, it was evident that although in the main, as shown by the analysis made by Mr. G. S. Blake under Professor Dunstan's supervision, it consisted of the oxides of thorium and uranium, its composition is by no means simple. The analyses referred to were made by Dr. R. D. Denison, by Mr. Gimingham, and by Mr. Le Rossignol; they are as follows (for convenience of reference Mr. Blake's analyses are also appended):—

	Denison.	Gimingham.	Le Rossignol.	Dunstan and Blake.		
				1.	2.	3.
Thorium oxide, ThO_2	76·4	77·52	77·07	72·24	76·22	78·86
Cerium oxide, Ce_2O_3 ?				6·39	8·04	1·02
Lanthanum oxide, La_2O_3				0·51		
Didymium oxide, Di_2O_3						
Uranium oxide, U_3O_8	14·9	13·23	12·95	11·19	12·33	15·10
Ferric oxide, Fe_2O_3	6·1	2·79	2·77	1·92	0·35	0·46
Lead oxide, PbO	2·0	3·42	2·41	2·25	2·87	2·59
Calcium oxide, CaO	—	—	—	—	—	1·13
Zirconium oxide, ZrO_2	—	—	—	3·68		
Loss on ignition	—*	1·63	1·63	—	—	0·20
Helium, He	—	—	—	—	—	0·39
Residue on fusion with $HKSO_4$	0·7	2·02	2·60	0·41	0·12	
	100·1	100·61	99·43	98·59	99·93	99·75

* Ignited mineral analysed.

The extraction of radiothorium by Dr. O. Hahn,* and various other investigations carried on in my laboratory, made it evident that under the heading "lead," for example, various other metals were included, and Dr. Büchner undertook to carry out an analysis on a larger amount, so as to ascertain what elements were present in the analytical groups into which the constituents of the mineral had been roughly divided by previous

* 'Jahrb. f. Radioaktivität,' vol. 2, 1905.

analysts. Another of the objects of his research was to determine how the radio-activity of thorianite is distributed over its various constituents. Assuming, as looks more than probable, that the radio-active constituents of thorianite, like those of similar radio-active minerals, are in process of change, it is to be expected that by working on comparatively large quantities these bodies and their products can be identified, even though in themselves they may not display the property of radio-activity.]

The methods employed in the chemical analysis of thorianite, together with the results obtained, will form the first section of this account, and the second part will deal with experiments relating to the radio-activity of the several fractions into which the mineral was separated.

The total quantity of mineral taken for analysis was 24·373 grammes. On treatment with concentrated boiling nitric acid the greater part of it dissolved. After decantation, the residue was once more boiled with fresh acid, and only a small quantity remained insoluble. The solutions were then mixed, evaporated to dryness, heated to 130° to render any silica present insoluble, and redissolved in dilute hydrochloric acid. The residue, which was dried, ignited, and weighed, was non-volatile on treatment with hydrofluoric and sulphuric acids; on testing it, it proved to be zirconium oxide, which had separated out as a basic salt.

Sulphuretted hydrogen was then passed through the hot liquid; the precipitated sulphides were treated with a solution of sodium sulphide, in which a portion dissolved. The residue dissolved almost completely in dilute nitric acid, only a trace remaining, which was soluble in *aqua regia;* after excess of acid had been removed by evaporation it was dissolved in water, and could be reprecipitated by sulphuretted hydrogen. Its amount, however, was too small to prove undoubtedly that it was mercuric sulphide: mercury, however, has been found (by Miss Evans) in residues from a larger amount of mineral.

Sulphuric acid was added to the nitric acid solution, and the precipitated lead sulphate was filtered off, dried, and weighed.

Ammonia was then added to the filtrate; this should have precipitated bismuth as hydroxide; the colour of the precipitate, however, was reddish-brown, and it was practically insoluble in hydrochloric acid; its quantity was also too small to permit of further investigation.

Copper was then precipitated by Rivot's method by addition to the filtrate of ammonium sulphocyanide, after reduction with sulphurous acid. The filtrate from the cuprous sulphocyanide gave traces of a brown precipitate with sulphuretted hydrogen, not in the least resembling cadmium sulphide.

The solution of the sulphides in sodium sulphide, which should have contained arsenic, antimony, and tin, and other elements capable of forming sulpho-salts, was analysed according to the methods of Bunsen and Clarke. A large excess of sulphurous acid was added to the liquid, and it was boiled for a long time. Arsenic is dissolved, antimony and tin remain behind. The insoluble residue was then suspended in water; ammonium persulphate and oxalic acid were added, and sulphuretted hydrogen was once more passed through the solution. After a repetition of this operation, the solution should have contained only antimony, and the residue, tin. The antimony sulphide, after excess of sulphur had been removed by carbon disulphide, had an almost black colour, probably due to the presence of selenium, which has been discovered by Professor Ogawa in this laboratory, in course of work on larger quantities of residue.

The solution, which was supposed to contain arsenic, was treated with sulphuretted hydrogen; to the precipitate, after solution and oxidation, ammonia and magnesia mixture were added, but no arsenate came down. On passing sulphuretted hydrogen, however, a small quantity of a black substance was precipitated.

To the filtrate from the sulphuretted hydrogen group ammonia was added after oxidation. The precipitate was redissolved in hydrochloric acid and, after adding a little concentrated nitric acid, a solution of oxalic acid was poured into the solution. The oxalates of the rare earths separated in a granular state, and were separated by filtration. This precipitate was then treated, according to Brauner's method, with a solution of 20 grammes of ammonium oxalate in 40 grammes of water, and boiled for about 10 minutes; the liquid was then diluted with about 800 c.c. of water. The thorium remains in solution; the ceria, etc., are precipitated. This process was repeated, and the solution was then evaporated to dryness and ignited; the thorium oxide was then weighed. The original solution in hydrochloric acid, however, still contained thorium and cerium; it was, therefore, partly evaporated and neutralised with ammonia, and oxalic acid was again added; the precipitate obtained was treated in the same way as has been already described. No attempt was made to separate ceria from the other earths, though they were present, as is proved by the red-brown colour of the Ce_2O_3.

The ammonia-group further contained iron, aluminium, and uranium, which are not precipitated by oxalic acid. They were separated by the usual methods; if the solution contains excess of ammonium carbonate, only iron and aluminium are precipitated by ammonium sulphide, and uranium is left in solution; after precipitation by evaporation, and re-solution in dilute

hydrochloric acid, it was thrown down by ammonium hydroxide and weighed as U_3O_8. The aluminium and iron were separated by treatment with excess of caustic potash.

The filtrate from the ammonia-group was evaporated to dryness in a platinum basin, and the ammonium salts were expelled; the residue dissolved almost entirely in hydrochloric acid (residue ω; see experiments on radioactivity). After neutralisation of the excess of hydrochloric acid, calcium oxalate was precipitated; the filtrate was again evaporated, and heated to redness. A residue was left, which was weighed, and submitted to several tests. Part of it dissolved on boiling with concentrated hydrochloric acid; the solution was evaporated, diluted with water, and treated with excess of caustic soda; the resulting precipitate was soluble in hydrochloric acid. After neutralisation, sodium phosphate gave a white precipitate (ϕ); on addition of ammonia to the filtrate, another precipitate came down in very small quantity (magnesia). The solution, which contained excess of soda, was evaporated and heated; on dissolving in water, a residue was left, soluble in hydrochloric acid, and precipitable by hydrogen sulphide with a brownish-red colour. None of these precipitates have been investigated more closely.

The portion of the mineral insoluble in nitric acid was fused with hydrogen potassium sulphate; the fused mass dissolved almost completely in hot water; on addition of a little hydrochloric acid, however, a precipitate was formed. After this had been removed by filtration, a further quantity of a white substance separated. Sulphuretted hydrogen was passed through the filtrate from this second precipitate, when a red-brown precipitate was thrown down, which was treated in the same manner as described for the soluble part of the mineral. Mercury was again present in traces, as well as substances which came down in place of bismuth and cadmium; these were probably identical in nature with those found in the other portion. After the supposed cadmium had been filtered off, the solution was evaporated and heated; a residue was left (ρ). The ammonia-group consisted only of aluminium, iron, and uranium. To the filtrate from this group ammonium carbonate was added; no precipitate came down, until after 24 hours, when a white substance separated. The filtrate left no residue after it had been evaporated and heated.

The precipitate mentioned above, which was obtained by adding hydrochloric acid to the solution of the fused mass, was once more fused with bisulphate, and dissolved in hot water (solution γ); a residue remained, which was partly soluble in concentrated hydrochloric acid (solution α), and a white residue was left. Sulphuretted hydrogen was then passed through

solution α, and after 24 hours' standing, a brownish-red precipitate was formed, the filtrate from which was mixed with solution β, obtained in the following way:—The solution γ had become turbid, and deposited a white precipitate; this was removed by filtration. Sulphuretted hydrogen was passed through the filtrate, and gave a precipitate similar in appearance to that formed in solution α; after filtering and allowing to stand, saturated with sulphuretted hydrogen for 24 hours, another quantity of what was apparently the same substance was obtained. The mixed solutions α and β were then oxidised, precipitated with ammonium hydroxide, and the precipitate dissolved in dilute hydrochloric acid. No precipitate was produced with ammonium oxalate, but only a slight turbidity, which passed away on addition of a few more drops. The oxalic acid was removed from this solution by evaporation and ignition, and the oxide was weighed. Qualitative tests showed that it consisted of oxide of titanium with traces of oxide of zirconium.

A separate quantity of the mineral was heated to redness, in order to determine the loss on ignition. It proved to be considerable, and chiefly due to the presence of water. The gas evolved was collected over mercury, and the carbon dioxide absorbed with caustic potash; the only other gas present was helium. From 1 gramme of the mineral 8·2 c.c. of helium were obtained at normal temperature and pressure.

The results of the analysis are given in the table (p. 390), where the measurements of radio-activity of the various precipitates are also given, contrasted with that of the mineral taken as 100.

For determining the radio-activity of the precipitates, a month was allowed to elapse after they had been obtained; about 10 milligrammes of the substance, if as much was available, was weighed out and placed in an electroscope. It was sometimes necessary, however, to place precipitate and filter together in the electroscope. The time in which the leaf moved over 20 divisions of the scale was noted, and from this the number of divisions per hour was calculated, allowance having been made for one hour's leakage, had exactly 10 milligrammes been placed on the copper plate. The figures thus obtained are given in the third column of the table, and in the second column the activity of the total quantity of the precipitate, obtained by multiplying the numbers in the third column by the weight of the substance, is recorded. The last column shows the percentage activity, that of the original mineral being taken as 100.

The mineral possesses 83·3 per cent. of the activity of standard uranium oxide, a sample several years old. It is also to be noticed that the activity is associated almost entirely with the soluble part of the mineral; while the

	Per cent.	Total activity.	Activity per 10 milligrammes.	Activity: mineral = 100.
Soluble portion.				
HgO	traces	284	Not weighed	
PbO	2·42	7206[1] 8360[2] 9570[3]	125 145 166	1·9 2·2 2·5
CuO	0·06	10		
SnO_2	0·05	none		
Sb_2O_4	0·11	16		
Bi_2O_3 ?	0·21	2153	414[4] 421[5]	— 0·6
As_2O_3 ?	traces	72		
CdO ?	,,			
Fe_2O_3	2·05	17,530[6] 21,380[7]	351 428	4·6 5·7
Al_2O_3	0·15	none		
U_3O_8	13·13	24,915[8] 35,490[9]	78 111	6·6 9·4
ThO_2	70·96	216,190	125	57·2
Ce_2O_3	1·96	8680[10] 9650[11]	178 198	2·3 2·6
ZrO_2	0·23	924	165[12] 163[13]	0·2
CaO	0·13	1080[14] 1225[15]	343 388	0·3 0·3
Residue	1·50	6590	—	1·8
Insoluble portion.				
HgO	traces	49		
Bi_2O_3 ?	0·15	124	44 and 16[*]	
CdO ?	traces			
Fe_2O_3	1·30	664[16] 1010[17]	21 32	0·2 0·3
Al_2O_3	0·06	none		
U_3O_8	0·02	21	40	
ZrO_2	traces			
TiO_2	0·45	none		
Unknown substance	0·040	66		
P_2O_5	traces	none		
CO_2	0·10			
He	0·15			
H_2O	3·20			
	98·84			75·7 80·3

Original mineral 155
Standard uranium oxide 186

Dates.—[1] 6 Feb.; [2] 27 Feb.; [3] 23 Mar.; [4] 8 Feb.; [5] 24 Mar.; [6] 13 Feb.; [7] 5 Mar.; [8] 15 Feb.; [9] 6 Apr.; [10] 16 Feb.; [11] 28 Mar.; [12] 8 Feb.; [13] 28 Mar.; [14] 14 Feb.; [15] 27 Mar.; [16] 13 Feb.; [17] 13 Mar.

* This precipitate came down in two portions, which were filtered off and kept separate; the first had the smaller activity.

ratio of the weights of the soluble to the insoluble portion is 40 to 1, the ratio of the activities is about 300 to 1. Again, comparing the activity of constituents common both to the insoluble and soluble portions, such as iron oxide, and bismuth (?) oxide, the samples from the soluble portion are much more active than those of the insoluble portion. In the case of iron the ratio is 17 to 1.

Nearly all the precipitates obtained from the soluble portion proved to be radio-active, although some had only a very slight effect on the electroscope. A remarkable exception is furnished by the alumina, which, although closely

allied to the strongly active iron group, is absolutely inactive. The active constituent of the iron group is therefore insoluble in excess of caustic potash; as further experiments showed, it gives off an emanation, the rate of decay of which, although not accurately determined, appears to point to its being due to that of radiothorium, separated by Hahn,* which always comes down with iron.

The activity of several precipitates had not reached a maximum at the last measurement; those of lead, iron, uranium, cerium, and calcium were still increasing, while the activity of bismuth (?), thorium and zirconium did not change. On the other hand, several precipitates showed activity originally, which decreased and even disappeared, *e.g.*, ω, insoluble in hydrochloric acid† (see p. 388). When originally obtained, it was placed in the electroscope along with its filter, and showed an activity of 30,000 to 40,000. After destroying the filter, and dissolving the precipitate with *aqua regia*, and evaporating the solution to dryness, the activity had decreased to 250, and it seemed then to be permanent at that value. It may be assumed, therefore, that this precipitate is a so-called X-substance; its chemical behaviour somewhat resembles that of a platinum-metal. After evaporation, the solution in *aqua regia* left a yellow crystalline residue, which turned black when gently heated. This black residue was insoluble in hydrochloric acid, but soluble in *aqua regia*; the solution showed again the same properties.

The next most active precipitate was found in the filtrate from the ammonia-group. Several very active minute traces of substance were collected on filters. The substance ϕ, mentioned on p. 388, obtained by addition of sodium phosphate, weighed only 8 milligrammes, and had a total activity of 3400, which increased to 3900 after standing for six weeks. Although this precipitate forms only 0·02 per cent. of the total weight of the mineral, it possesses 1 per cent. of the total activity. In connection with this it may be remembered that Rutherford,‡ during his early experiments on thorium and thorium-X, also found a strongly active constituent in his thoria, precipitable by sodium phosphate after removal of the thoria. He was not always able to detect it, however, and ascribed it to the presence of an impurity in commercial thoria.

In conclusion, it is my pleasant duty to express my hearty thanks to Sir William Ramsay for his kind assistance and advice.

* 'Jahrb. f. Radioaktivität,' vol. 2, 1905.

† The residue, ρ (p. 388), was also initially very active, but lost its activity in a short time.

‡ 'Chem. Soc. Trans.,' vol. 81, p. 345.

Experimental Investigation as to Dependence of Gravity on Temperature.

By L. SOUTHERNS, Whitworth Scholar.

(Communicated by Professor W. M. Hicks, F.R.S. Received September 13,—Read November 8, 1906.)

Few experiments have been made with a view of detecting with accuracy any alteration in the weight of a given substance which may accompany variation of its temperature. The recent experiments of Professor Poynting and Mr. Phillips described in the 'Proceedings of the Royal Society,' September 13th, 1905, led to a null result.* At the time of the publication of this result the Author had been engaged for about a year on a similar line of research, and as the two methods of experiment were entirely different, it was thought advisable to continue with this work in order that the results obtained by the two methods might be compared. Further reference will be made to this matter in the sequel; but it may be noted here that in their experiments a mass of gunmetal was heated externally, while in the present ones a mass of paraffin oil was heated internally.

Original Apparatus and Method of Experiment.

The apparatus in its original form was constructed several years ago by Dr. Hicks. It consisted of a specially made balance, carrying at one end of the beam a calorimeter, and at the other end a magnetic counterpoise. The calorimeter consisted of a light aluminium vessel containing refined paraffin oil, in which was immersed a coil of fine platinum wire of about 1100 ohms resistance, wound on a mica frame. Two other aluminium vessels surrounded the inner one, and the spaces between them were packed with cotton wool; the vessels themselves were made airtight by sealing up with wax. Leads from the coil passed up a tube to the suspension pieces of the calorimeter. A magnet was suspended from the other end of the beam as counterpoise, so that by passing a small current through a coil fixed in the balance case the magnet could be attracted or repelled, and the balance thus brought to its zero position and calibrated while within its closed case.

The beam consisted of two parallel brass arms fastened together by means of a block of insulating material. The knife-edges were of hardened steel,

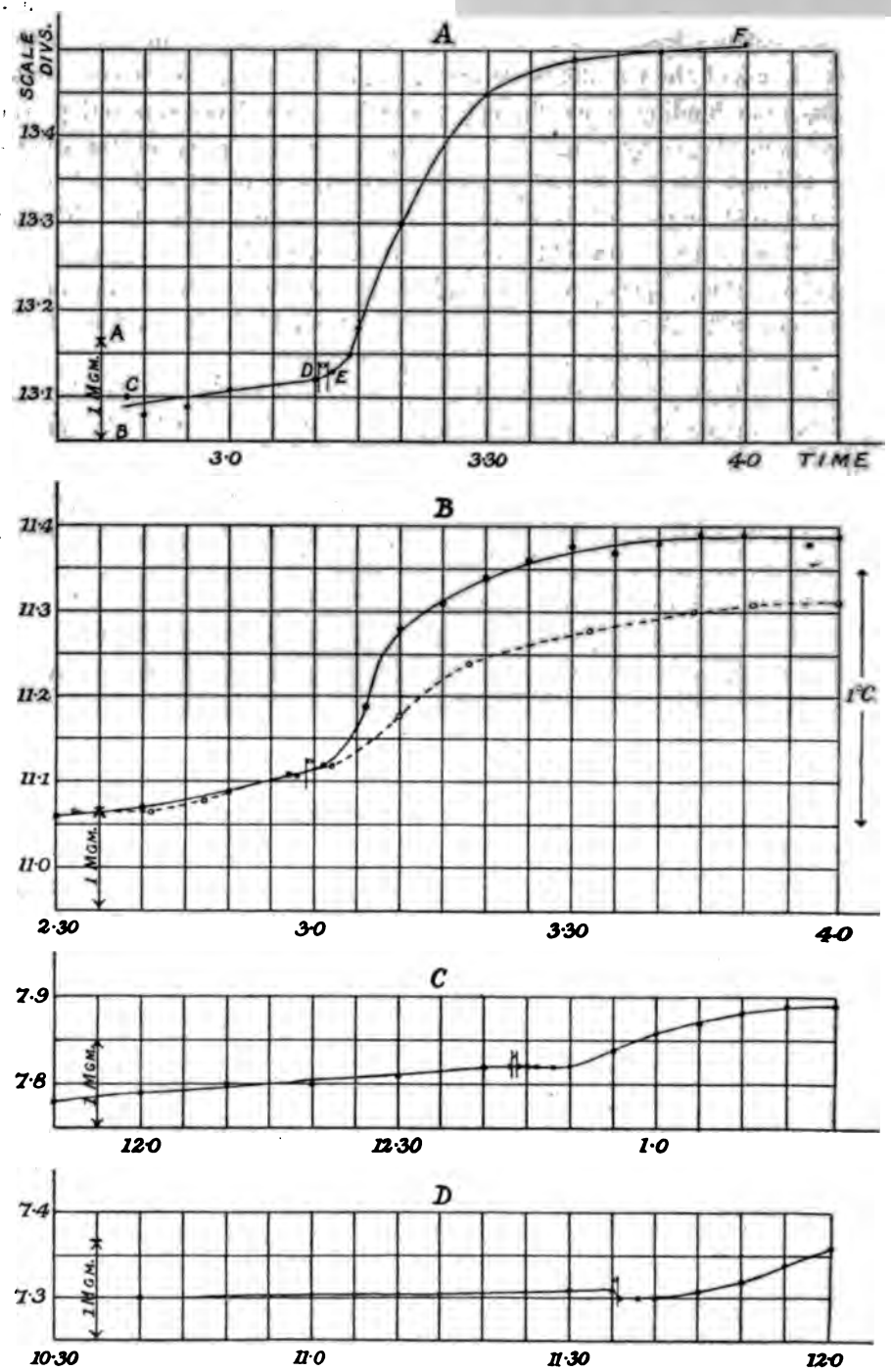
* It is interesting to remember that Count Rumford attempted this experiment, and concluded from its negative results that heat could not consist of a ponderable fluid (*cf.* 'Life and Works of Count Rumford,' vol. 3, p. 1).

and they rested on steel plates which were connected to binding screws outside the balance case. Each knife-edge was electrically connected to the centre of one of the parallel brass arms of the beam; thus a current could pass from one binding screw through the knife-edge and one conducting arm of the beam, thence by a steel point to the suspension piece of the calorimeter, through the heating coil immersed in the mass of oil, and back again through the other part of the beam and its knife-edge to the other binding screw. The heating coil could also be used as a platinum thermometer for ascertaining the temperature of the oil before and after the passage of the heating current. A mirror fixed to the beam enabled observations to be made from a distance by means of telescope and scale.

The advantages of this design of calorimeter and method of heating are that the heating is very rapid; that it takes place while the balance is swinging on its knife-edges; and that the outer envelope of the calorimeter is not heated, and only slowly becomes warm, so that air currents, etc., are reduced to a minimum. Also, the complete experiment can be conducted from a distance by the observer.

A number of experiments were made with this apparatus, using a heating current of about 0·2 ampère, alternating. The diagram A shows the results of a typical experiment plotted in the form of a curve, the abscissæ of which represent times and the ordinates scale readings, *i.e.*, deflections of the balance beam. The length of the vertical line A B in the diagram represents an increase of weight of 1 milligramme, the weight of oil heated being about 250 grammes. During the period C D observations were taken previous to heating, the balance being left free to swing on its knife-edges. D E represents the period of heating (one minute in this case), and E F part of the period of cooling, during which observations were also taken.

In all these experiments a large apparent increase of weight took place very soon after the period of heating, although the changes during the heating were very small. In order to investigate the cause of this, a platinum thermometer was inserted in the balance case near the calorimeter, and its temperature observed from time to time during an experiment. Diagram B shows the temperatures indicated plotted to the same time base as the balance deflections. The ordinates of the temperature curve (shown dotted) are proportional to the temperatures indicated, and approximately represent in magnitude the diminution in the buoyancy of the air, supposing the air surrounding the calorimeter to be at the temperature indicated by the thermometer. This is, of course, only a rough approximation to the truth, but the general similarity of the curves indicates that the effect is largely due to diminution of buoyancy of the air caused by escape of heat from the


A
SCALE DIVS.
13·4
13·3
13·2
13·1
A
B
C
D
E
F
1 MGM.
3·0
3·30
4·0
TIME
B
11·4
11·3
11·2
11·1
11·0
1°C.
1 MGM.
2·30
3·0
3·30
4·0
C
7·9
7·8
1 MGM.
12·0
12·30
1·0
D
7·4
7·3
1 MGM.
10·30
11·0
11·30
12·0

calorimeter. As the temperature of the oil was only raised four or five degrees in these experiments, it was obvious that this effect must be greatly reduced before trustworthy observations could be made of any change in weight which might occur during the heating period if considerable increments of temperature were to be used. It was then decided to make the weighings in a partial vacuum in order to reduce this buoyancy effect.

Modifications of the Apparatus.

After some preliminary trials with a temporary vacuum chest, the apparatus was rearranged and set up in a constant temperature room in the basement of the new Physical Laboratory at Sheffield. This room was for the purposes of this experiment divided into two portions by a partition, the balance being set up on one side and observations taken from the other. The general arrangement of the apparatus is shown in fig. 1. In the figure

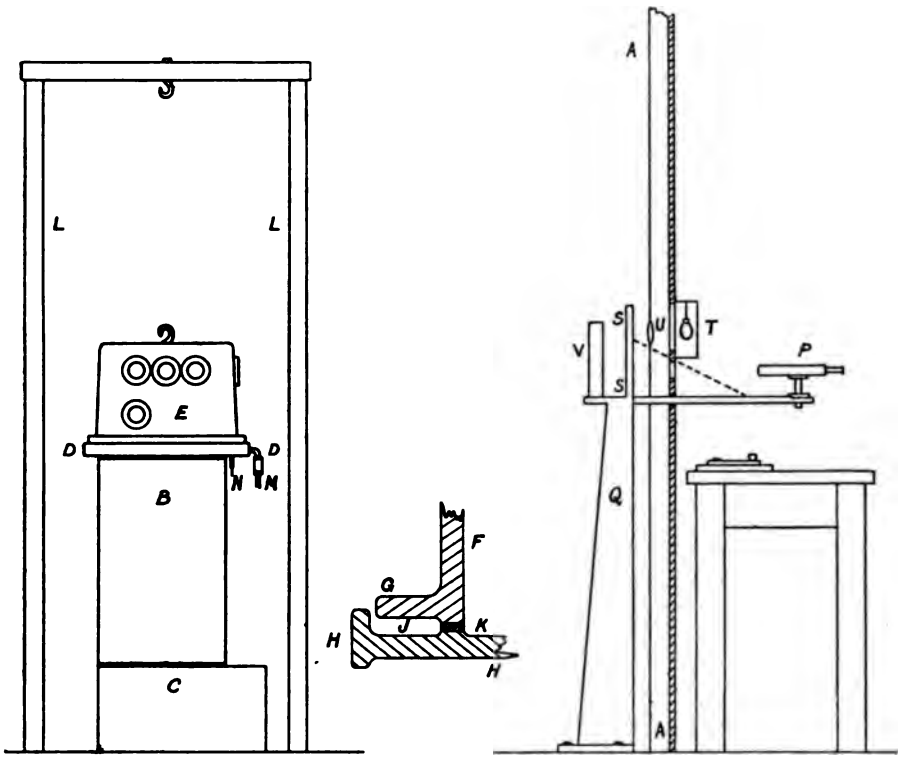


FIG. 1.

A A represents the partition, to which are fixed various instruments, resistances, etc., not indicated in the figure. B is a brick pillar, which has a rubber course at its base, resting on a concrete slab C. The balance

is placed on a cast-iron tray D D, and over it is lowered a cast-iron cover E provided with circular windows. The bearing surfaces of cover and tray are faced with rubber, and the joint is rendered airtight by pouring mercury around it. An enlarged section of this joint, which can be made and broken with the greatest ease, is given in the figure. F shows a portion of the cover with its strengthening flange G, H the tray, J the mercury space, and K the rubber facings. Returning to the main figure: L L represents a trestle from which pulleys are slung for raising the cover E. M is a tube to which are connected a water pump and a Fleuss air-pump for exhausting the balance case, and also a gauge which indicates the stage of exhaustion. Copper wires, sealed into glass tubes, which are in turn sealed into holes through the tray D, form the electrical connections for conveying the current into the balance case; one of these is shown at N. P is the observing telescope fixed to a stand Q set up inside the portion of the room cut off by the partition so as to be free from sudden variations of temperature, vibration, etc. The scale is placed at S S, and is illuminated by means of a lamp T, with lens U, and mirror V. Many instruments and practical details are left out of the figure in order to avoid complication.

It was also necessary to construct a new calorimeter, as the original one was not designed to support the internal pressure produced when the balance case is exhausted. This is shown in fig. 2, which will be described in due course. Also a closed vessel having a volume equal to that of the inner vessel of the calorimeter was attached to the magnetic counterpoise.

The new apparatus was first tested at full atmospheric pressure, a current of 0·35 ampère being used for heating. It was found that motions of the balance were produced by the passage of the current; thus deflections of 0·3 to 2·5 mm. were observed while the current was passing, but the balance nearly resumed its original position when the current was cut off. About 60 experiments under varied conditions were made in order to ascertain the causes of these disturbances. They were found to be due to induced currents, chiefly in the magnetic counterpoise coil, to self-induction in the beam and other parts of the circuit inside the balance case, and to some source of error due to the passage of the current through the knife-edges. It was, therefore, necessary to make further alterations in the apparatus. The magnetic counterpoise had to be sacrificed, and the current was made to pass by two stout copper wires fixed near each other to the beam, instead of by the brass arms of the beam, which enclosed a considerable area. These wires were pointed and made to just dip into two mercury cups attached to the supports of the balance so that the points of contact of wire and mercury were in the same straight line as the central knife-edges. The

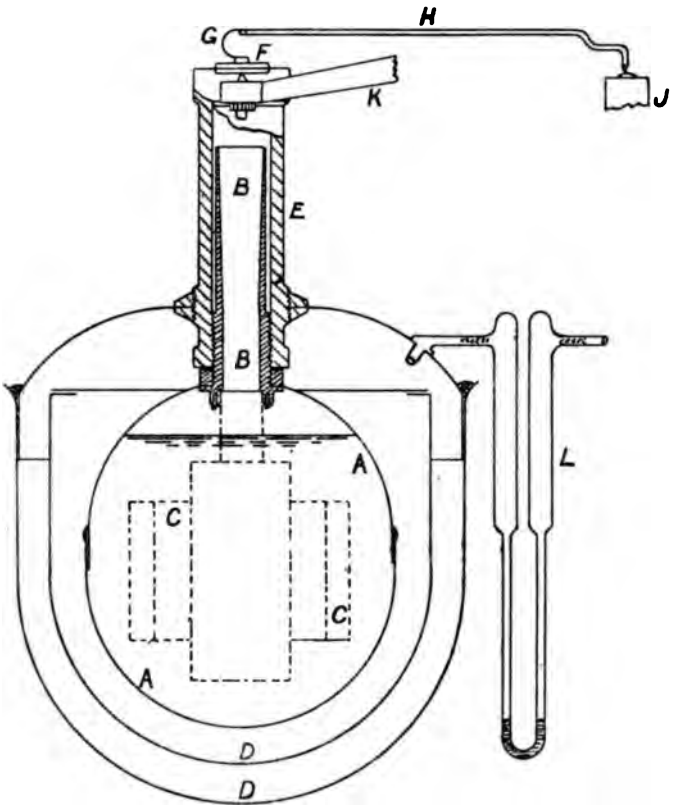


FIG. 2.

A A. Copper calorimeter, 9 cm. × 8 cm., made in two halves soldered together, containing oil to about the level shown. Weight of the copper = 53 grammes; of the oil 233 grammes; of the total heated mass, including solder and coil, about 300 grammes.

B B. Brass tube soldered to top of calorimeter. The leads from coil pass up this tube, which is sealed airtight with khotinski cement.

C C. The dotted lines indicate shape of frame on which the fine platinum wire coil is wound (non-inductively). The wire is distributed fairly uniformly throughout the mass of the oil.

D D. Aluminium vessels packed with cotton wool. The outer one is airtight, but the inner one is not.

E. Ebonite tube, closed at top, which retards loss of heat from B B, and carries the suspension plates.

F. Suspension plate, with glass bearing slip underneath. One lead from coil is attached to F.

G. Tinfoil strip connecting F to the conducting rod for conveying current to the coil.

H. Conducting rod fixed rigidly to beam by an ebonite clip not shown.

J. Mercury cup attached to balance case into which the pointed end of H dips to make contact with external circuit. The point is in same straight line as knife-edges.

K. Part of beam with bearing point.

F, G, H, J, K are in duplicate.

L. Gauge (not shown in its true position) containing mercury. This allows air to be drawn from the spaces between A D D when the balance case is exhausted, but the thread of mercury falls back and prevents escape of residual air from calorimeter during an actual experiment.

calorimeter terminals were connected to these wires by tinfoil strips. These precautions almost entirely did away with the disturbances. The arrangements are shown in fig. 2.

The counterpoise was also provided with an external vessel and gauge like that of the calorimeter.

With the modified apparatus a series of observations was taken, the pressure of air in the balance case ranging from 1·6 to 5·0 cm. of mercury. In one case 6 mm. was used, but a discharge took place within the balance case, fusing the tinfoil strips. In this particular case the pressure was reduced by means of a bulb containing cocoanut charcoal, connected to the exhausting tube and cooled by liquid air. The low vacuum, however, not sufficiently insulating the leads, the method was not repeated.

Final Experiments.

The table (p. 399) gives a record of the final experiments made with the modified apparatus. Observations were taken for a considerable period before and after heating; the curves showing some of these are given in the diagrams indicated by letters in the last column of the table.

It should be noted that all the deflections marked in the table are temporary only (except No. 8) and the balance righted itself in one or two minutes in all cases. This effect plainly could not be due to an actual difference of weight due to alteration of temperature, or it would have persisted longer, for the fall of temperature in two minutes was very small—always less than 1° C. Experiment No. 8 is abnormal, no doubt some accidental disturbance took place. In calculating x in Column 9 the temperatures given in Column 7 have been used. The calculation is as follows:—

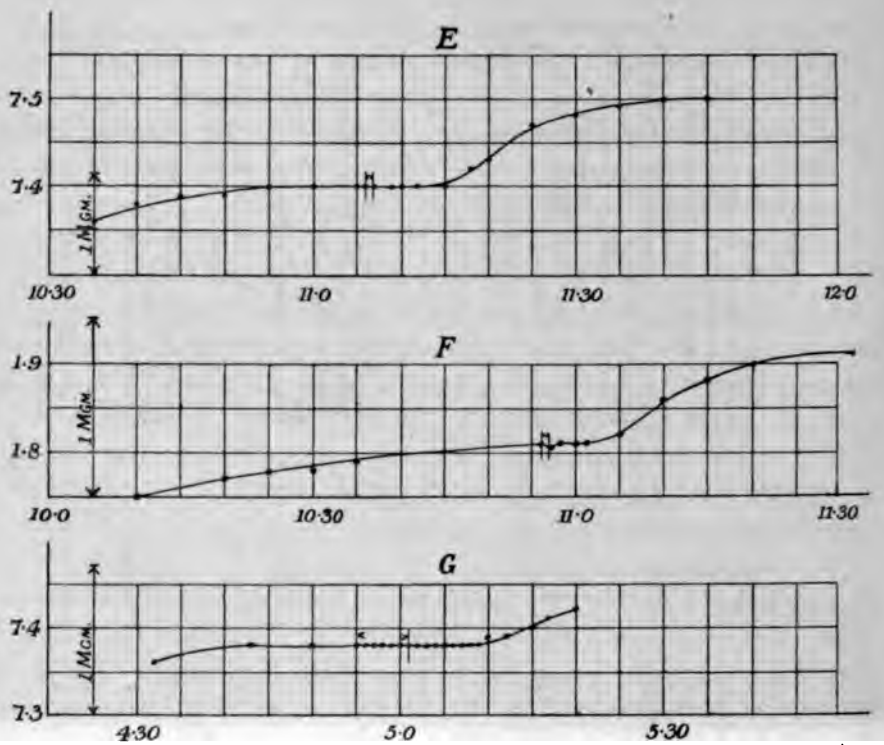
Total weight heated = 300,000 milligrammes.
1 scale division corresponds to n milligrammes (Column 8);
$\therefore$ 1 „ „ to 1 in $300{,}000/n$;
$\therefore$ 1/10 „ „ to 1 in $3{,}000{,}000/n$;

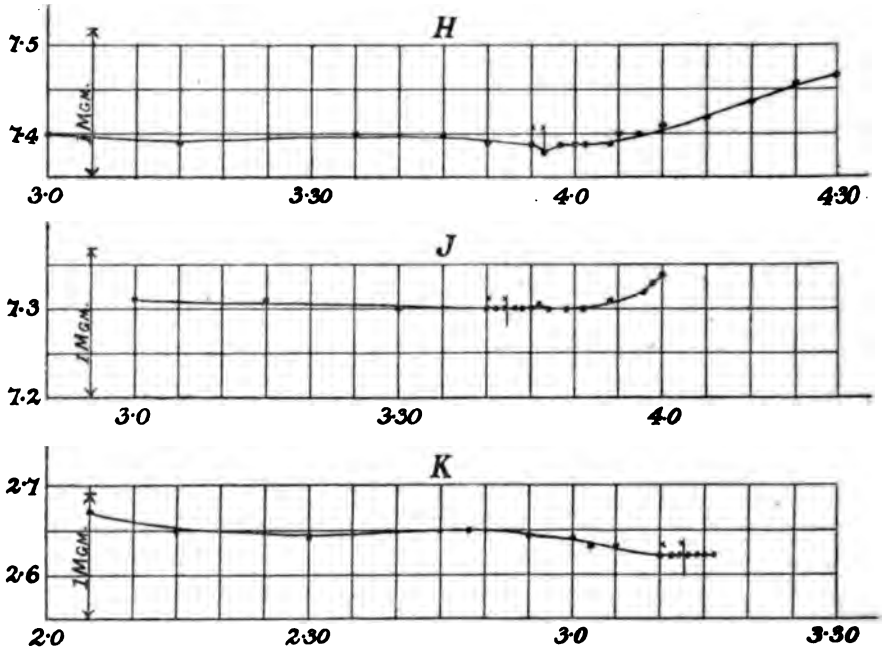
and if rise in temperature = $\theta°$, 1/10 scale division corresponds to 1 in $(\theta \times 3 \times 10^6)/n$ per degree rise of temperature, and as this is the smallest measurable deflection, we have $x = (3\theta/n) \times 10^6$.

In nearly all cases a very slight oscillation of the beam took place during the passage of the current.

It seems reasonable to assume from the results of these experiments that any variation of weight which may occur is less than 1 part in 10^8 per degree rise of temperature. The fact that all the small displacements observed were

1. No. of experiment.	2. Date.	3. Pressure in balance case.	4. Current (alternating).	5. Time of passage of current.	6. Rise of temperature by platinum thermometer.*	7. Rise of temperature by specific heat of the oil.*	8. Sensitiveness of balance, 1 mm. of scale = n milligrammes.	9. Smallest measurable alteration of weight expressed as 1 part in x of total mass heated, per degree rise of temperature.	10. Alteration of weight during heating, in millimetres of scale. + = increase, − = decrease.	11. Alteration of weight during heating, expressed as 1 part in y, per degree rise of temperature.	12. Time, after cutting off current, taken by balance to resume its former position.	13. Remarks. * The temperatures were taken by using the heating coil as a platinum thermometer, and by calculation from the known heating effect and specific heat of the oil. The difference is probably due to non-uniformity of heating, as well as to an actual difference of temperature between the wire and the liquid in which it is immersed. Δ in Column 10 indicates a quantity too small for measurement.	14. Refer to the curves marked with these letters.
	1906.	cms. of Hg.	amps.	secs.	°C.	°C.	n.	x.	mm.	y.	mins.		
1	May 30	2·5	0·35	30	11·8	9·0	1·0	$2·7 \times 10^7$	0	—	—	No effect.	C
2	„ 31	1·6	0·35	30	11·8	9·0	1·0	$2·7 \times 10^7$	0	—	—	„	
3	June 11	1·6	0·35	30	11·8	9·0	1·0	$2·7 \times 10^7$	− Δ	—	1	Minute temporary deflection.	
4	„ 16	—	—	—	—	—	—	—	—	—	—	Experiment spoiled by mercury in Gauge L, fig. 2, going over.	
5	„ 22	1·9	0·35	30	11·8	9·0	0·7	$3·8 \times 10^7$	0	—	—	No effect.	
6	„ 23	1·9	0·35	30	11·8	9·0	0·7	$3·8 \times 10^7$	− Δ	—	1 to 2	Minute temporary deflection.	
7	July 23	3·2	0·35	30	11·8	9·0	0·86	$3·1 \times 10^7$	0	—	—	No effect.	
8	„ 24	2·4	0·35	45	—	13·5	0·86	$4·7 \times 10^7$	− 0·1	$-4·7 \times 10^7$	10	Bad result. The only one which gave a permanent deflection with heating.	D
9	„ 25	2·6	0·35	60	22·5	18·0	0·86	$6·3 \times 10^7$	0	—	—	No effect.	E
10	Aug. 2	—	—	—	—	—	—	—	—	—	—	Experiment spoiled as in No. 4.	
11	„ 3	2·7	0·35	50	—	15·0	0·5	$9·0 \times 10^7$	− Δ	—	1	Minute temporary deflection.	F
12	„ 4	2·6	0·35	60	22·5	18·0	0·5	$1·08 \times 10^8$	− 0·1	$-1·08 \times 10^8$	2	Small temporary deflection.	
13	„ 9	3·5	0·35	60	22·5	18·0	0·49	$1·1 \times 10^8$	0	—	—	No effect.	
14	„ 14	4·6	0·15	360	—	20·0	0·6	$1·0 \times 10^8$	0	—	—	„	G
15	„ 15	3·8	0·31	90	22·8	21·1	0·6	$1·05 \times 10^8$	− 0·1	$-1·05 \times 10^8$	1	Small temporary deflection.	H
16	„ 16	3·9	0·27	140	26·4	25·2	0·6	$1·26 \times 10^8$	0	—	—	No effect.	J
17	„ 17	5·0	0·27	170	32·5	30·6	0·72	$1·27 \times 10^8$	0	—	—	„	K


E
7·5
7·4
1 MGM.
10·30
11·0
11·30
12·0
F
1·9
1·8
1 MGM.
10·0
10·30
11·0
11·30
G
7·4
7·3
1 MGM.
4·30
5·0
5·30


H
7·5
7·4
1 MGM.
3·0
3·30
4·0
4·30
J
7·3
7·2
1 MGM.
3·0
3·30
4·0
K
2·7
2·6
1 MGM.
2·0
2·30
3·0
3·30

in one direction has given rise to the suggestion on the part of Dr. Hicks that while no permanent effect is produced by rise of temperature, it is just possible that the body may be slightly lighter during the actual development of heat. The present apparatus, however, is inadequate for the investigation of these minute effects; some of them may be due to motions in the oil itself during the process of heating.

*Comparison of Results with those of Poynting and Phillips.**

A few words may be said with regard to the two methods employed. The chief differences are, first, in the Birmingham experiments a much higher vacuum is employed; secondly, the mass is of gunmetal, and is heated by means of an external steam jacket, and, thirdly, two experiments have to be performed, one with a solid mass and one with a hollow one, and the difference between the results taken, whereas in the present method only one is needed to give the complete result.

The advantages gained by the internal method of heating are, first, the actual experiment itself is completed in two or three minutes, whereas in the external method two experiments, lasting 8 to 48 hours each, are required, during which time the balance is swinging on its knife-edges. This gives time for various disturbances due to external causes to interfere with the results of the observations. Secondly, the external envelope of the calorimeter does not sensibly rise in temperature during the critical part of the experiment, and there is no necessity to use a high vacuum in the balance case. This means that radiometer effects are not brought into play (as is the case in the other method), whilst air currents are, nevertheless, practically or entirely absent. Thirdly, the balance case, supports, beam, etc., do not become heated, therefore there is no connection such as that which has to be applied on this account in the case of the external heating method.

In the experiments of Poynting and Phillips, the result is given as no variation of weight within 1 part in 10^9 per degree rise of temperature, while in the present paper a degree of accuracy of 1 in 10^8 only is recorded. The Author, however, thinks that in point of delicacy the present experiments are probably at least equal to the above, on account of the fact that no corrections need to be applied to the results. It would appear to be extremely difficult to apply satisfactory corrections for alterations of temperature of the balance case, and this has had to be attempted by them, on account of the considerable length of time occupied by an experiment. On December 8, 1904, for example, the correction curve appeared to be 17 times as steep as on the day before. Fig. 3 is plotted from the table on

* 'Roy. Soc. Proc.,' A, vol. 76, September 13, 1905.

p. 451 of the paper referred to and gives the correction for the hollow mass. The observations made on particular days are connected by dotted lines. The firm line shows the gradient deduced from the points marked by the method of least squares—the application of this method, however, would appear to be superfluous in this case on account of the irregular disposition of the points. The nature of the diagram will show how uncertain such a correction must be. Also, the gradient is deduced from observations lying between 12°·7 C. and 15° C., but it is applied to all temperatures from 10°·45 C. to 17°·45 C.,* *i.e.*, over a range three times as great as that for which the observations for the correction were made. At the higher and

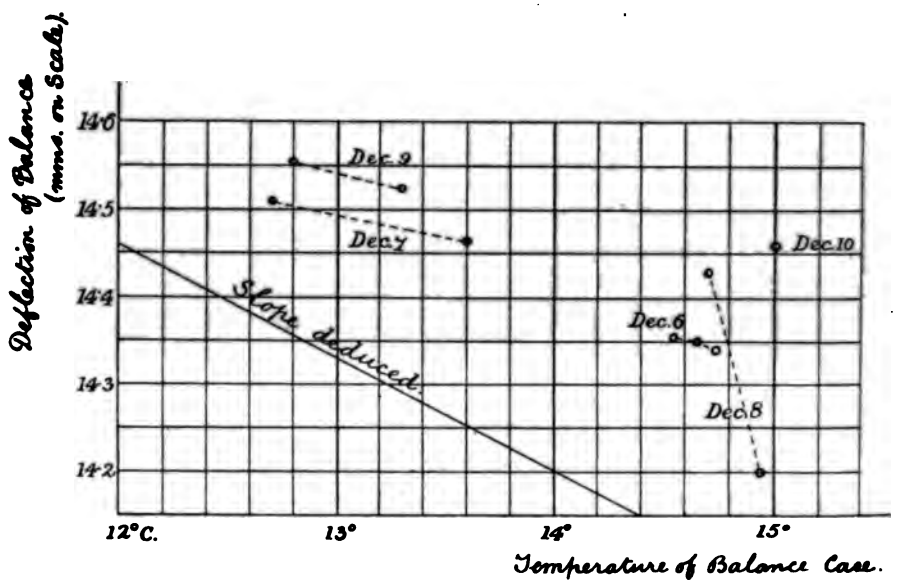


FIG. 3.

lower temperatures the corrections must be still more uncertain. In some cases the correction deduced from a mean curve like that shown in fig. 3 (it being impossible to obtain a fresh correction curve for each experiment) amounted to over 60 times the final actual result (1 in 6×10^9) and in many cases to over 30 times this amount.

Again, it is impossible to measure directly the temperature of the gun-metal masses, and it appears probable that these would not assume the extreme temperature of the jacket, especially in the case in which cooling by liquid air was employed, when the time allowed for cooling was rather short.

* 'Roy. Soc. Proc.,' September 13, 1905, p. 453. There is evidently a misprint on line 3 of this page, which should read: Correction for temperature of case −0·13 division per 1°·1.

The vacuum between the jacket and the mass would act as an efficient non-conductor of heat.

We may, however, probably conclude with considerable certainty on the combined testimony of the two series of experiments that, within the limits of temperature used, no variation of weight occurs greater than 1 part in 10^8 for a rise in temperature of 1° C.

Note on the Continuous Rays observed in the Spark Spectra of Metalloids and some Metals.

By W. N. Hartley, D.Sc., F.R.S.

(Received October 17,—Read November 8, 1906.)

In a paper published in the 'Proceedings of the Royal Society,'* reasons were given for believing that the back-ground of continuous rays in the spark spectra of the metalloids, for instance, tellurium, arsenic, antimony, and bismuth, was caused by the light emitted by an incandescent oxide, whether in a state of vapour or solid, having its origin in the cooling of the dense vapour of the element in an atmosphere containing oxygen. The spectra of metals which are not oxidisable did not show it, namely, gold, silver, and platinum, neither did those of the easily volatile metals such as mercury, indium,† thallium, zinc, and cadmium. It was visible on photographed spectra of metals belonging to the iron group, but at the points of the electrodes only, where a non-volatile oxide is formed.

As the original explanation has not been accepted as satisfactory‡ I have recently submitted the question to a special examination.

It must not be overlooked that spark spectra with continuous rays are yielded by the metals lead, tin, and cadmium, if the exposure of the photographic plate be increased to double that sufficing for the line spectra, and that sparks passing between electrodes of these metals in air deposit their oxides on all objects near to them; in hydrogen, films of metal are deposited on the walls of the containing vessel, and when air is substituted for hydrogen there is at first a deposit of oxide, and subsequently one of

* Vol. 49, pp. 448—451, 1891.

† This word is misprinted "iridium" in the 'Proceedings.'

‡ See Kayser's 'Handbuch der Spectroscopie,' vol. 2, p. 286; also P. Lenard, 'Annalen der Physik,' 1905, vol. 17, pp. 208—212.

metal when the oxygen has been exhausted. In 1905, having again sought for the most convenient source of a continuous spectrum extending as far into the ultra-violet as wave-length 2144, the subject of the continuous rays was re-investigated by passing sparks between metallic electrodes in a closed vessel containing different gases. The conditions of the experiment, such as the size of the electrodes, the length of spark, and the period of exposure were identical for each gas and for each metal. The exposure was five minutes in a spectrograph with quartz lenses of 20 inches focus, and Cadett and Neall's spectrum plates developed with ferrous oxalate. The spectra were taken, one below the other, on the same plate, and close together so that they could be easily compared. The results shortly are as follows:—The emissive power of *cadmium*, as measured by its action on a photographic plate, stands first in hydrogen, second in nitrogen, third in air, and fourth weak in carbon dioxide. This order applies particularly to the lines, but if we consider the continuous rays, the spectrum in hydrogen is the strongest, then those in nitrogen and air are about equal, but less strong than in hydrogen, the spectrum in carbon dioxide is very feeble. The result appears different when the electrodes are of *lead*. Thus the emission spectra both of lines and continuous rays are equal and very strong in hydrogen and nitrogen: they are equal, but very feeble, in carbon dioxide and air. The [illegible] lines are a little stronger in nitrogen than in hydrogen, the continuous spectrum in both is strong and of equal intensity: the lines in carbon dioxide show less intensity, and the continuous spectrum is of about half the intensity of that in the hydrogen and nitrogen; in air the lines and the continuous rays are both enfeebled. In order to ascertain whether the metalloids give stronger spectra of continuous rays when they are exposed to the influence of hydrogen, arsenic and antimony were experimented upon. It is necessary to quote only the case of arsenic. It became of interest to ascertain whether by the action of the spark on this element in hydrogen a characteristic hydride could be obtained which would prove a definite test for its presence. The results showed that the lines are very sharp and distinct in hydrogen while the continuous rays are feeble, but with air the lines are more feeble while the continuous rays are practically non-existent, or at most barely visible in any part of the spectrum. The result was similar with antimony. No evidence of any importance was obtained showing that the spectrum was other than that of arsenic or antimony as observed in the spectrum of air.

On reviewing the facts we see, first, that the nature of the gas [illegible] the electrodes appears to have a distinct influence on the spectra, and that it operates somewhat differently on different metals; [illegible]

continuous spectrum is not caused by oxidation, because in every case it is strongest when the electrodes are immersed in hydrogen or nitrogen. All the spectra are weakest in an atmosphere containing oxygen, whether free or combined, such as air or carbon dioxide, and the conclusion is inevitable that oxidation destroys or weakens the spectrum, for even in the carbon dioxide atmosphere the reversible interaction $CO_2 \rightleftarrows CO + O$ may liberate oxygen in greater quantity than that which is present in the same volume of atmospheric air. The continuous rays are clearly not due to the emissive power of any incandescent oxide, either gaseous or solid.

On the Use of Metallic Electrodes as a Source of Continuous Rays.—Particulars of trials made with various metallic electrodes were given on p. 473 of the 'Phil. Trans.,' Part II, 1885 ("Absorption Spectra of the Alkaloids,") and need not be recapitulated.

E. Pauer also experimented in the same manner 12 years afterwards and arrived at the same conclusion, namely, that the continuous rays of cadmium answered the purpose better than copper, iron, or nickel electrodes.*

At various times a number of flame spectra have been examined, as, for instance, those of sulphur and of phosphorus burning in oxygen, of carbon disulphide in nitrous oxide, phosphine in oxygen, ether and hydrogen with oxygen burnt from a blowpipe, also acetylene with oxygen burnt in the same manner. The inverted Welsbach incandescent gas-light used without a glass, the zirconia, magnesia, and lime lights have all been tried. Of the flame spectra the best effect is obtained with acetylene and oxygen, the rays are quite continuous and of equal intensity from the red to beyond wave-length 2700. There are some difficulties attending manipulation with flames, particularly on account of their great heating effect, and I have therefore returned to the use of the cadmium spark spectrum for special observations on the spectra of hydrocarbon vapours, with results that I propose to make the subject of another communication.

* 'Wiedemann's Ann.,' 1897, vol. 61, p. 363.

The Refractive Indices of Water and of Sea-water.

By J. W. GIFFORD.

(Communicated by W. A. Shenstone, F.R.S. Received May 9,—Read June 28, 1906.)

1. *Method of Observation.*—Measurements of the refractive indices of water have been made by Fraunhofer, Gladstone, Van der Willigen, Dufet, Pulfrich, and many others. Those now offered were made by the new method previously described.*

2. *Instruments.*—In addition to the instrument used for measuring the refractive indices of fluorite quartz and calcite,† a larger goniometer has been employed, especially for determining the temperature-refraction coefficients and for the critical part of the work generally. This instrument has quartz objectives of 3 inches diameter and 27·5 inches focal length, and quartz-calcite objectives of 2·375 inches diameter and the same focal length, and it has a divided circle of 18 inches diameter. There are two micrometers with reading microscopes, one on each side of the circle. These micrometers are similar to that of the smaller goniometer before described,† and readings were taken in the same way. The hollow prism (by Hilger) used to contain the water has a clear aperture 1·675 inches by 2·375 inches, and is entirely of quartz. It can be used on either instrument (see Appendix).

3. *Temperature.*—A standard thermometer, interchangeable with the stopper, was kept with its bulb in the water during each measurement and, subject to the precautions for maintaining an approximate temperature of 15° C. before described,† readings were taken at the commencement and at the close of each measurement, and the mean taken. In no case did the variation between these exceed 1° C. By means of the temperature-refraction coefficients, which were found in both cases for three wave-lengths, the coefficients for the other wave-lengths were interpolated, and all the indices in the table corrected for a mean temperature of 15° C.

4. *Material.*—I am indebted to the kindness of Mr. W. R. Bousfield for the special examples of distilled water used. That for the experimental work on the variation of index due to impurities was supplied in a platinum bottle, that for the remainder of the work in a large bottle of special green glass, but little soluble. One cubic centimetre of this latter evaporated in a polished silver dish left a slight residue which was shown by subsequent experiment to have little effect on the index. For the specimen of sea-water

* 'Roy. Soc. Proc.,' Feb. 13, 1902. † *Loc. cit.*

I am indebted to Lieutenant E. R. G. Evans, R.N., who took it in blue water, 5 miles south of the Royal Sovereign Lighthouse (off the coast at Eastbourne). It was surface water and was collected in another large glass bottle of the same kind.

5. *Standard Wave-lengths.*—Rowland's have again been adopted whenever possible.

6. *Measure of Error.*—This is the same as already described.* The approximate estimate made from group deviations is as follows:—

Water.—There are 26 measurements in the table, in

5	of which a	=	less than	$\frac{3}{4}''$	corresponding value of index	= 0·0000025
11	„	=	„	$1\frac{1}{3}''$	„ „	= 0·0000050
8	„	=	„	$2\frac{2}{3}''$	„ „	= 0·0000098
1	„	=	more than	2″·861	„ „	= 0·0000098
1	„	=	as much as	$5\frac{1}{2}''$	„ „	= 0·0000202

Sea-water.—There are 12 measurements in the table, in

5	of which a	=	less than	$\frac{3}{4}''$	corresponding value of index	= 0·0000025
5	„	=	„	$1\frac{1}{3}''$	„ „	= 0·0000050
1	„	=	„	$2\frac{2}{3}''$	„ „	= 0·0000098
1	„	=	as much as	2″·688	„ „	= 0·0000103

Owing to the additional difficulties, especially with sea-water, the accuracy is not so great as with solid bodies; but these indices may be taken as correct to the fourth decimal place, and it is believed that in all cases the error does not exceed 0·000025, and in most is not more than 0·000015.

Appendix.—Special experimental work. In order to determine the disturbing effect due to the double refraction of the quartz plates forming the sides of the hollow prism, at the suggestion of Dr. Glazebrook a complete measurement was made on the large goniometer, and then, each plate having been rotated through 180° in its own plane, another complete measurement of index for the same wave-length (line E) was made. The results, reduced to 15° C., were as follows:—

Plates normal.	Plates rotated through 180°.
1·3356125	1·3356185

Want of parallelism in the faces of the plates was tested for by registering the position of the image of the slit (collimator and telescope being in line) without a prism, and then interposing the empty prism in its normal position and noting the effect. The difference of position of the image was not measurable.

To determine the extent and influence of impurities in solution, a specimen

* *Loc. cit.*

of ordinary distilled water, kept in an ordinary glass bottle, a cubic centimetre of which gave considerable deposit on evaporation, was measured.

Mean result, reduced to 15° C. = 1·3355798.

Table of Refractive Indices at 15° C.

Wave-length.	Water.	Sea-water.
7950·0 Rb	1·32855	
7682·45 K_α(A′)	1·329183	1·335652
7065·59 He(B′)	1·330443	1·33689
6563·04 H_α(C)	1·331562	1·338062
5893·17 Na(D)	1·333433	1·339959
5607·1 Pb(A)	1·334289*	1·340938
5270·11 Fe(E)	1·335643	1·342296
4861·49 H_β(F)	1·337501	1·344260
4678·35 Cd	1·338515	1·345315
4340·66 H_γ(G′)	1·340723	1·34763
3961·68 Al	1·343959	1·350928†
3610·66 Cd	1·347915	
3302·85 Zn	1·352699	"
3034·21 Sn	1·358337	
2748·68 Cd	1·36675	1·37494
2573·12 „	1·37390	
2445·86 Ag′	1·380979	
2312·95 Cd	1·389262	
2265·13 „	1·39309	1·402880
2194·4 „	1·39937	Absorption begins
2144·45 „	1·40455	Absorption
2098·8 Zn	1·409702	„
2062·0 „	1·414543	„
2024·2 „	1·41996	„
1988·1 Al	1·425663	„
1933·5 „	1·4361	„
1852·2 „	Absorption	„

Note.—The number of figures in each index indicates the estimated freedom from errors of observation. The following interpolated indices are in all probability more correct for those referred to:—* 1·334294 † 1·35094.

A specimen of the special distilled water referred to, kept in a platinum bottle and prepared in platinum vessels, 1 c.c. of which, when evaporated in the silver dish, left a just perceptible residue, was then measured—

Result, reduced to 15° C. = 1·3356359.*

This specimen was then boiled and measured again—

Result, reduced to 15° C. = 1·3356338.

* There is a difference of reading for line E, resulting in 0·0000076 in the index between the two goniometers used, which it was difficult to account for. On testing the division of the two circles by readings from various zero points, I find that the large one stands the test almost up to the unit in the sixth place of decimals in the value of the index, while the smaller just begins to show discrepancy at five places: thus it is the smaller circle that is in fault. The experimental measurements here given were made on the large goniometer, but, for the sake of uniformity with previous measurements of index,

Finally, the same specimen was frequently agitated with air while standing for a week, and three measurements were then made—

Mean reduced to 15° C. = 1·3355777.

During the measurements of sea-water the prism was emptied and refilled for every complete measurement to prevent errors due to rise of density from evaporation and to the displacement of the sides by salt crystals.

Temperature Refraction Coefficients.

Wave-length.	Water.	Sea-water.
5893 (D)	−0·0000801	−0·0000785
2748	—	−0·0000747
2265	—	(−0·0000758)
2145	−0·0000724	
1988	−0·0000687	

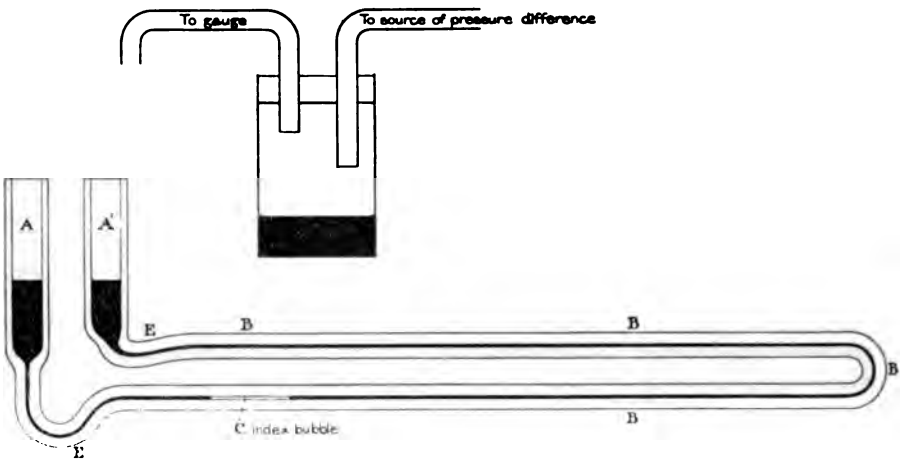
all those given in the table have been made on the smaller instrument. But they agree well with other observers. The index for the mean D line in the table is 1·333433. This, brought to its value at 20° C. by use of the temperature coefficient, becomes 1·333032. Dufet ('Recueil de Données Numériques,' vol. 1, p. 83) gives the mean value of the measurements of this line at 20° C. by 29 observers as 1·33303.

On a Compensated Micro-manometer.

By Bertrand J. P. Roberts.

(Communicated by Sir John I. Thornycroft, F.R.S. Received August 14,—Read November 8, 1906.)

The accompanying sketch shows a form of fluid-pressure gauge or micro-manometer, intended for use as an anemometer and for the indication and measurement of small pressures.*



Ratio : approximately 10 : 1 diameter of bores.

A design for a sensitive pressure gauge, or micro-manometer. Anti-evaporative attachment for use with volatile fluids ; one should be connected in series with each side of the gauge—only one shown. A Woulff's bottle with three necks would be a convenient substitute. Cal. chlor. tube should be used also in case of hygroscopic fluid in gauge.

The two limbs A and A′ of a U-tube are connected by a tube of finer bore B, and this tube B contains an index bubble—preferably of air, C, the bends at E form a trap, to prevent the accidental loss of the bubble. The small separate part is an arrangement for preventing loss by evaporation in the case of volatile fluids—it does not need description. The sensitiveness of the gauge obviously depends on the ratio between the bores of the limbs and the connecting tube—this is approximately 10 : 1 in the example shown ; also to some extent on the fluid employed in the gauge, and the fluid used should depend on the intended application and on the degree of sensitiveness desired.

* The feature in which this arrangement differs from Sir W. Siemens' bathymeter is the compensation.

The length of the index bubble C should be approximately equal to the distance between the centres of the limbs A, A′; it will then be found that the gauge is practically indifferent to changes of position or level, as the effect of the air bubble (while in the *lower* horizontal tube) will counteract the effect due to any change of level of the limbs A and A′; it is, of course, not possible to exactly compensate for this, as the length of the bubble will vary slightly with the temperature and the barometric pressure. Any tendency to error in the readings from these two last-mentioned causes can be obviated by observing both ends of the index bubble; but, as it is not necessary to read very minutely, owing to the multiplying effect, this source of error can generally be neglected.

It is not advisable to employ a larger bore for the tube B than 2 mm., and 1½ mm. is preferable, as the surface tension is insufficient (with most fluids) to prevent fluid from passing the air bubble in larger bores; the limit to the smallness of the bore depends on the viscosity of the fluid and the rapidity of readings desired. For the same reasons it is not practicable to use pure water as the working fluid, as owing to its high surface tension the zero point is very indefinite; water *can* be used, however, if some substance, such as glycerine or calcium chloride, is added to lower the surface tension.

The writer cannot say definitely what is the limit of sensitiveness that can be reached—this depends on the resistance offered by the surface tension and viscosity of the fluid to the motion of the index bubble—making its movements very slow, so that in returning to zero it may take five minutes or more, with a very sensitive form—using alcohol. To reduce this effect as much as possible it is necessary to use either alcohol or ether (and perhaps pentane) for the most delicate results.

The air bubble acts practically as a piston, and no fluid can be seen to pass it at a normal rate of movement, but fluid can be caused to pass in a thin film if the bubble is forced to move rapidly. There seems to be a critical speed—for each size of bore and fluid—above which the surface tension is unable to overcome the adhesion of the fluid, to the walls of the tube, quickly enough.

In connection with this I have noticed an interesting effect—showing well the rapidity of the motion of fluid in the centre of tubes, and the almost stationary condition of the layer next the sides.

If a small bore—say 2 mm.—tube, similar to the gauge described above, and containing an air bubble, filled with uncoloured alcohol, be taken, and some coloured alcohol is added to one limb, then the air bubble moves at the average velocity of the fluid, but the coloured alcohol entering the tube will

be seen to be drawn, or rather pushed, out in a long conical point, moving much more rapidly than the bubble, and eventually overtaking it and turning over; the fluid at the sides will be still quite uncoloured until mixed by diffusion; to a certain extent the effect is reversible, and the cone of coloured alcohol can be drawn back without mixing very much.

The device shown for preventing evaporation should be in duplicate, one to each limb; only one is shown, as an example.

On the Hygroscopic Action of Cotton.

By Orme Masson, D.Sc., F.R.S., and E. S. Richards, B.Sc.

(Received June 25,—Read June 28, 1906.)

In an earlier paper by one of us* an account was given of the behaviour of dry cotton-wool when immersed in air saturated with water vapour, and the relation between the hygroscopic absorption and the change of temperature which the cotton manifests was investigated. It was shown that, so long as the surrounding air is saturated, the absorption process appears to be unending, though its velocity continuously diminishes; or, in other words, true equilibrium between such an atmosphere and cotton wool, however moist, appears to be impossible, just as it would be impossible between the same atmosphere and an aqueous solution, however dilute. It was pointed out, however, that "if placed in an atmosphere containing water vapour at anything less than saturation pressure (*e.g.*, in the open air) the cotton would in time reach a state of equilibrium, either by absorption or by evaporation, according to its initial condition." As we could find no record of any complete investigation of such relationship, it seemed desirable to determine the amounts of vapour absorbed by a given quantity of cotton in atmospheres of various known degrees of humidity. This has been done; but it has been found necessary to determine the true equilibrium values by approaching them from both sides, by absorption and by evaporation, since neither process becomes really complete in any practicable time, though each leads in a few hours to what might be mistaken for true equilibrium.

Reference must here be made to the interesting work published by Clayton Beadle, in 1894 and 1895,† which was unfortunately entirely

* 'Roy. Soc. Proc.,' vol. 74, pp. 230—254.

† 'Nature,' vol. 49, p. 457; 'Chem. News,' vol. 71, p. 1; *ibid.*, vol. 73, p. 180.

overlooked by Masson until his attention was called to it after publication of the paper already referred to. Beadle seems to have been the first to observe the striking elevation of temperature that dry cotton undergoes when exposed to damp air and to study the progress of absorption and the course of the temperature change. He, however, did not use atmospheres of constant and known humidity and temperature, but used the open air of the laboratory, so that his curves are affected by considerable irregularities. Apart from these, his results are in general character similar to those we have since obtained.

The experimental method employed by us in this investigation was similar to that already described by one of us.* The cotton-wool employed was the purified material sold as "absorbent" and was washed several times with boiling distilled water before being used. A suitable quantity, after drying, was wound round the bulb of a thermometer, which was provided with a rubber stopper that closed a jacket-tube in which it could be weighed. By means of this stopper the thermometer could also be inserted into a tube in the cover of a desiccator containing phosphorus pentoxide. It was proved that 24 hours' exposure in this desiccator sufficed to bring the cotton to a constant weight, and this method of drying was adopted throughout in preference to the heating method previously used, as it was suspected that frequent heating to above 100° might cause some alteration in the condition of the cotton. The atmosphere of known humidity was obtained in the following way. A glass jar of about 1500 c.c. capacity was provided with a plate-glass cover, ground and lubricated to fit accurately, and a short wide tube was cemented vertically through a central opening in the cover. A cylindrical porous pot of nearly 500 c.c. capacity (cleaned by many previous extractions with acid) was fixed by rubber wedges inside the jar so as to leave a clear space around and below it. The glass jar and porous pot were filled with sulphuric acid solution of known strength, covered, and placed in a thermostat of such depth that only the top of the tube in the cover showed above the water level. The jar was weighted with lead so as to keep it steady when submerged, and the water of the thermostat had free circulation all round and underneath it. Before an experiment the porous pot was emptied by a siphon operating through the central tube, which then served for the admission of the cotton-covered thermometer and also a duplicate instrument without cotton, which was always treated simultaneously and served as a counterpoise in weighing. These were suspended from fixed hooks and could be read accurately to at least a twentieth of a degree by means of a telescope with a micrometer scale.

* *Loc. cit.*

The interior of the porous pot was kept constant as to humidity by evaporation from its walls, through which filtration of acid occurred, but this infiltration was slow enough to allow of the thermometer hanging for more than 24 hours without risk of the liquid reaching the cotton-wool. The exact strength of the sulphuric acid in each experiment was determined by taking the density of the sample pipetted from the pot, the percentage strength being then read from a curve drawn from Pickering's values for the same temperature.* This being known, the corresponding vapour pressure was read from a curve drawn with percentage of H_2SO_4 as abscissæ and relative vapour pressure (that of water at the same temperature taken as unity) as ordinates. Regnault's values† were used in constructing this curve, and they were supplemented by the very concordant values obtained by a different method by Helmholtz.‡ Such a curve, drawn for 20° C., is practically correct also for all neighbouring temperatures, as the relative vapour pressure of a given acid solution is almost constant.

Two sets of apparatus were kept in alternate use so that each porous pot could soak for several days in a new acid solution before tests were made with it. A third apparatus was reserved for distilled water so as to provide a saturated atmosphere when required.

The sulphuric acid employed for making up the solutions was subjected to a preliminary treatment for complete removal of oxides of nitrogen. Unless this is done, the cotton is to some extent affected by exposure over the higher strengths of acid; it tends to become brittle and its hygroscopic power is sensibly diminished.

For convenience, our results are discussed in the sequel under six heads.

1. *The Determination of the Conditions for Equilibrium.*—In order to ascertain the weight of absorbed moisture which puts a given weight of cotton into true equilibrium with an atmosphere of given humidity, it is not sufficient to expose the dry cotton to the action of that atmosphere till its weight becomes apparently constant, for the rate of absorption, which rapidly diminishes, becomes almost inappreciable, while the absorption itself is certainly incomplete. This is proved by supersaturating the cotton by previous exposure over water or a more dilute acid and then again immersing it in the original atmosphere. It now loses moisture by evaporation till it once more attains an apparently constant weight; but this is considerably greater than that previously reached by absorption. The thermometer on which the cotton is wound serves the useful purpose of indicating the

* 'Chem. Soc. Trans.,' vol. 57, pp. 152—156.

† Quoted in 'Carnelley's Tables,' vol. 11, p. 750.

‡ 'Wied. Ann.,' vol. 27, p. 508.

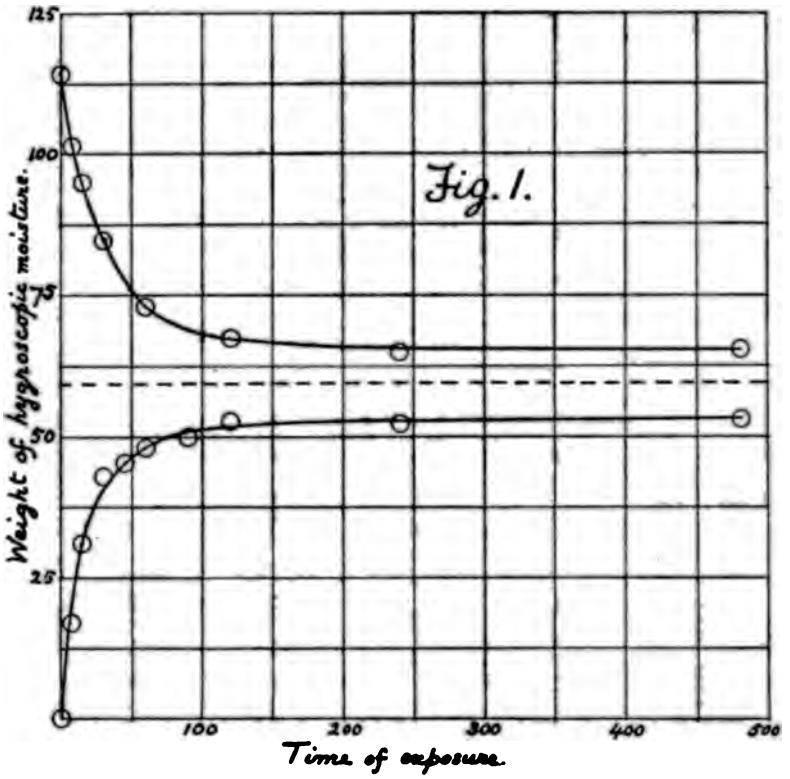
progress of either change; for during the absorption test it rises rapidly for a few minutes and then falls with diminishing velocity towards the temperature of the thermostat (as previously described),* and this process is reversed during the evaporation test when the thermometer falls quickly to a minimum and then rises with diminishing velocity towards the temperature of the environment. In order to render these indications accurate, it is necessary to suspend the thermometer protected by its jacket-tube in the apparatus for an hour or two before the test is begun, so that it may have the same temperature as the thermostat at the moment of exposure. The figures given in Table I and the corresponding curves (fig. 1) illustrate the characteristic behaviour of dry cotton and of supersaturated cotton. The acid used in these tests contained 40·5 per cent. of H_2SO_4, corresponding to a relative vapour pressure of 0·556. The acid strength was proved to remain constant throughout the series. Each point in the absorption and evaporation curves was obtained by an independent experiment. The excess moisture required for each evaporation test was imparted by exposure over water, the time necessary for imparting a definite quantity of moisture being read off from a curve drawn from previous experiments to show the course of absorption in a saturated atmosphere. It is possible in this way to predetermine the imparted moisture accurately to within

Table I.—0·948 gramme of cotton exposed over acid of 40·5 per cent. H_2SO_4. $p/P = 0·556$. Bath at 20° C.

Absorption tests.		Evaporation tests.	
Time of exposure (minutes).	Moisture absorbed (gramme).	Time of exposure (minutes).	Moisture retained (gramme).
0	0	0	0·1140
7·5	0·0170	7·5	0·1015
15	0·0312	15	0·0950
30	0·0430	30	0·0847
45	0·0453		
60	0·0480	60	0·0730
90	0·0500		
120	0·0526 0·0530	120	0·0674
240	0·0522	240	0·0648 0·0654
480	0·0530	480	0·0655

Mean value of absorption and evaporation results ..... 0·0601 at 120 minutes.
0·0586 „ 240 „
0·0592 „ 480 „

* *Loc. cit.*



about a milligramme. The quantity here used was rather less than double that indicated for true equilibrium, viz., 114 instead of 118 milligrammes.

As is seen from the results, this true equilibrium value must lie somewhere between the apparent limits of absorption and evaporation, and their arithmetic mean may be taken as sufficiently correct.

The time allowed for absorption or evaporation in any particular case has depended on the strength of the acid, and has varied from four hours in the driest to 24 in the most humid atmospheres employed, experience showing that longer exposure within practicable limits would not appreciably affect the results. As a rule, the initial moisture imparted before an evaporation test was about double that required for equilibrium; but any deviation from this rule produces no sensible difference in the final result, as it merely hastens or retards the initial evaporation and is thus in a measure self-compensating.

To avoid circumlocution, the following symbols are used in the sequel:—

W is the weight of dry cotton employed.

T is the temperature of the apparatus.

p is the actual pressure of water-vapour in the atmosphere employed.

P is the saturation pressure of water-vapour at the same temperature.

M_A is the weight of moisture absorbed by the sample of dry cotton of weight W after exposure in the apparatus till further absorption appears negligible.

M_E is the weight of moisture retained by the same sample after it has been supersaturated by exposure over water and then allowed to evaporate in the apparatus till further loss appears negligible.

M is the arithmetic mean of M_A and M_E, and is taken as indicating the amount of absorbed moisture which is required to establish true equilibrium.

2. *The Influence of Temperature.*—The M values obtained with a given sample of cotton depend on the strength of sulphuric acid over which it is exposed, but not upon the temperature. In other words, they depend upon the relative vapour pressure (the saturation pressure of water-vapour being taken as unity), and not on the absolute vapour pressure of the enveloping atmosphere, for the relative vapour tension of any given sulphuric acid solution is practically independent of the temperature. It seems, therefore, that cotton containing a definite proportion of moisture resembles an aqueous solution in that it also follows Babo's law, *i.e.*, exercises a vapour tension which is at different temperatures a constant fraction of that of pure water.

The following tests (Table II) illustrate this. They were all made with the same sample of cotton. It was subsequently shown to have been somewhat altered by previous exposure over impure sulphuric acid, and was

Table II.

(1) Acid of density 1·4245 at 25°; 53·5 per cent. H_2SO_4; $p/P = 0·30$.

T.	p.	M_A.	M_E.	M.
20°	5·2	27·5	28·9	28·2
25°	7·1	27·8	29·6	28·7
30°	9·5	26·5	28·0	27·2

(2) Acid of density 1·3340 at 25°; 44·0 per cent. H_2SO_4; $p/P = 0·49$.

T.	p.	M_A.	M_E.	M.
20°	8·5	40·5	42·4	41·4
25°	11·5	39·0	43·5	41·2
30°	15·5	39·5	41·5	40·5

(3) Acid of density 1·2818 at 25°; 38·0 per cent. H_2SO_4; $p/P = 0·615$.

T.	p.	M_A.	M_E.	M.
20°	10·7	47·7	52·3	50·0
25°	14·5	47·9	51·1	49·5
30°	19·4	47·8	51·7	49·8

therefore, not used in further work, but this does not affect the conclusions drawn here. The values of M are given in milligrammes and those of p in millimetres of mercury.

3. *If different quantities of the same quality of cotton* be employed, the weight of moisture required to establish equilibrium with an atmosphere of given humidity is in constant ratio to the weight of the cotton. In the following tests not only the weights of cotton-wool were varied, but also the mode of wrapping it, some samples being wound tightly and others more loosely round the supporting thermometer. This makes no sensible difference in the final M value, though, of course, it may to some extent influence the velocity of absorption or evaporation by affecting the freedom of access of the moist air to the surface of the fibres.

Table III.—Acid of density 1·1398 at 20° C.; 20·3 per cent. of H_2SO_4; $p/P = 0·874$; weights in grammes.

W.	M_A/W.	M_E/W.	M/W.
1·0228	0·1105	0·1329	0·1217
0·9480	0·1102	0·1319	0·1210
0·6227	0·1132	0·1361	0·1247
0·5165	0·1084	0·1332	0·1208
0·4680	0·1053	0·1357	0·1205

These results, taken in conjunction with those given in the last section, suffice to show that, for a given quality of cotton wool, the value of M/W depends only on that of p/P.

4. *The Influence of Surface.*—It is obvious that the weights of different samples of the same cotton wool, having the same average dimensions of fibre, are proportional to the extents of surface exposed to the hygroscopic action, and so that the constancy of the ratio M/W in their case gives no proof that M is really a function of the mass of cellulose rather than of its surface. It may, of course, be both. To test this question properly it is desirable to employ cellulose preparations having various known ratios of surface to mass. This is, however, not very easily done. The individual

fibres in any given bundle of cotton vary considerably, and only a very laborious microscopic examination could give a reliable estimate of the average dimensions. Moreover, for a fair comparison, all the samples would require similar previous treatment in order to obviate not only errors due to residual impurity, but also such unequal alterations of the cellulose molecule itself as are at least possible in the case of so complex a substance. For this reason, experiments with amorphous cellulose, obtained by one of the solution methods, might give results not fairly comparable with those from cotton fibre, even if all ordinary impurities were eliminated. Such experiments, if carried out with all precautions, might, however, afford information of value and help to settle the question of whether the surface film of moisture does, as suggested by one of us,* diffuse osmotically into the substance of the cellulose and form with it a solid solution. A few tests already made with pure filter paper may be cited. The paper used was Schleicher and Schüll's ash-free, No. 589. Three papers of 7 cm. diameter were wrapped tightly round the bulb of a thermometer and secured with a few turns of cotton thread, and then well washed and dried before use. The dry weight of paper (and thread) was 0·918 gramme. The M values were determined over three different strengths of acid, and may be compared with the corresponding values for cotton wool, which have been read from the curve shown in fig. 2. It will be seen that they are somewhat higher, weight for weight, in the case of the filter paper, but that the difference is not great.

Table IV.—Tests with Filter Paper.

W = 0·918 gramme; bath at 20° C.

Acid employed.			M_A.	M_E.	M.	Filter paper. M/W.	Cotton wool. M/W.
$d_{20°}$.	H_2SO_4 p. c.	p/P.					
1·3866	49·3	0·360	0·0410	0·0482	0·0446	0·0486	0·0456
1·2899	38·9	0·596	0·0582	0·0724	0·0653	0·0711	0·0676
1·1986	27·6	0·768	0·0827	0·0971	0·0899	0·0980	0·0920

5. *The relation between the moisture content and the vapour tension* of any given preparation of pure cotton may be shown by a curve, plotting M/W as abscissæ and p/P as ordinates. The experimental method employed is applicable over a large range, but becomes unworkable when p/P exceeds about 0·97, since there is in practice a limit to the time that can be given

* *Loc. cit.*

for absorption or evaporation over acid or for supersaturation over water as a preliminary to the evaporation test. It is, however, obvious that the method must in any case be inapplicable to that value of M (if there be one) which corresponds to the full saturation pressure, for exposure over water for any length of time would, at the best, give only M_A, which is less than M, and it would be impossible to supersaturate the cotton and then determine the M_E value by evaporation over water. These considerations support our previous contention that no true equilibrium is possible between cotton, however moist, and saturated aqueous vapour. In other words, the approach of the curve in fig. 2 to the saturation pressure is probably asymptotic. In this connection it is instructive to contrast the time-absorption curve in an unsaturated atmosphere (fig. 1) with that showing a 12-hours' absorption over water.*

The first series of experiments made for the purpose of testing the variation of M/W with p/P was spoilt by the use of insufficiently purified sulphuric acid, for it was found that the cotton had become brittle and so altered in the course of the work that points re-determined did not fall on the curve. A better result was obtained in the series given below. Here 15 different strengths of specially purified acid were used in the order indicated in the table, and the fact that the first two points determined lie practically on the curve formed by joining the later ones is sufficient guarantee that no appreciable change in the hygroscopic power of the cotton

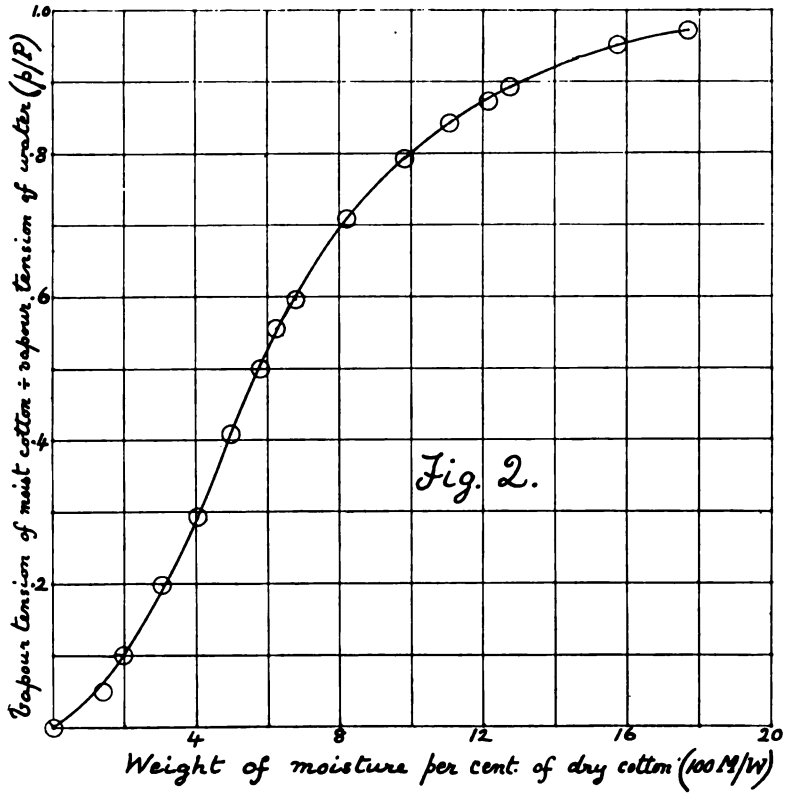
Table V.—Hygroscopic Tests with 0·948 gramme of Pure Cotton over Sulphuric Acid Solutions (at 20° C.).

Order of test.	Acid employed.			M_A.	M_E.	M.	M/W.
	$d_{20°}$.	H_2SO_4 p. c.	p/P.				
3	1·6516	73·8	0·050	0·0120	0·0145	0·0132	0·0139
4	1·5724	67·0	0·100	0·0175	0·0198	0·0186	0·0196
5	1·4850	59·0	0·198	0·0264	0·0311	0·0288	0·0304
6	1·4167	52·6	0·294	0·0356	0·0406	0·0381	0·0402
7	1·3672	47·2	0·408	0·0441	0·0497	0·0469	0·0495
8	1·3282	43·1	0·500	0·0509	0·0593	0·0551	0·0581
2	1·3028	40·5	0·556	0·0530	0·0655	0·0592	0·0624
9	1·2887	38·8	0·598	0·0599	0·0690	0·0644	0·0679
10	1·2368	32·3	0·710	0·0716	0·0840	0·0778	0·0821
11	1·1930	26·8	0·794	0·0860	0·1002	0·0931	0·0982
13	1·1616	23·2	0·844	0·0989	0·1107	0·1048	0·1106
1	1·1398	20·3	0·874	0·1045	0·1250	0·1148	0·1210
12	1·1226	18·1	0·894	0·1114	0·1300	0·1207	0·1274
14	1·0686	10·3	0·952	0·1378	0·1606	0·1492	0·1574
15	1·0378	6·2	0·972	0·1563	0·1792	0·1678	0·1770

* See 'Roy. Soc. Proc.,' vol. 74, p. 244.

occurred in the course of the work. The general form of the curve was quite similar in the first series, though the exact values were not trustworthy. It is obvious that such a curve indicates the relative water-vapour tensions of cotton of different degrees of moistness.

The numbers in the fourth and eighth columns of this table have been used in plotting the curve shown in fig. 2.



6. *A New Method of Hygrometry.*—The initial velocity with which any given sample of dry cotton wool absorbs moisture at the moment of its exposure must depend on the pressure of water-vapour in the atmosphere to which it is exposed and on conditions of surface, etc., which are constant for that particular sample. Now it has already been shown by one of us that the heat production is always proportional to the amount of hygroscopic absorption; and as, at the first moment of exposure, when the cotton is dry and at the same temperature as its environment, the heat produced may be regarded as entirely consumed in raising the temperature of the cotton, it follows that the initial rate of that rise is directly proportional to the

pressure of aqueous vapour. Adopting the same notation as in the previous paper, viz:—

t = time since exposure of the dry cotton,

θ = difference of temperature between the cotton and its environment,

m = weight of moisture absorbed,

p = pressure of water-vapour in the atmosphere surrounding the cotton,

we may express the above conclusions briefly thus:—

$$\left(\frac{d\theta}{dt}\right)_0 \propto \left(\frac{dm}{dt}\right)_0 \propto p.$$

Now it was shown* that the whole temperature curve, in the case of immersion of dry cotton in saturated vapour, is expressed with very fair accuracy by the equation

$$\theta\left(t+\frac{\tau^2}{t}\right) = 2\tau\phi,$$

where ϕ is the maximum value attained by θ, and τ is the corresponding value of t. Later results confirm this, and it follows that at any moment (t)

$$\frac{d\theta}{dt} = 2\tau\phi\,\frac{\tau^2-t^2}{(\tau^2+t^2)^2};$$

and therefore that

$$\left(\frac{d\theta}{dt}\right)_0 = 2\,\frac{\phi}{\tau}.$$

If this equation holds also for cases of immersion in unsaturated water-vapour, we arrive at the conclusion that ϕ/τ should be proportional to p, or that $\phi/\tau = kp$, where k is a constant for the particular sample of cotton, or rather for the instrument, which consists of the thermometer and its cotton covering

This conclusion is fairly justified by the following observations. The first set was designed to test the constancy of k when the air in the apparatus was saturated with water-vapour at different temperatures. The results are shown in the following table for temperatures between 15° and 35° C. Above 35°, k appeared to diminish; but considerable error is probably caused when there is a large difference between the temperature of the thermostat and that of the outer air, especially as a short exposure of the thermometer to the latter is unavoidable when it is being withdrawn from its jacket-tube before immersion.

The next series of tests was made with a different thermometer and covering of cotton wool. Eleven tests in air saturated with water-vapour at 20° gave for this instrument a mean k value of 0·140, the extremes being

* *Loc. cit.*

Table VI.—Dry Cotton-covered Thermometer ("F") exposed over Water at various Temperatures.

T.	p (mm. of mercury).	ϕ (degrees C.).	τ (minutes).	ϕ/τ.	$\phi/p\tau = k$.
15°	12·7	9·6	6·5	1·48	0·116
,,	,,	9·7	6·85	1·41	0·112
,,	,,	9·6	6·8	1·41	0·111
20°	17·4	11·25	5·65	1·99	0·114
,,	,,	11·55	5·6	2·06	0·119
25°	23·5	12·95	4·85	2·67	0·114
,,	,,	13·1	4·9	2·67	0·114
30°	31·5	14·25	4·05	3·52	0·112
,,	,,	14·0	4·1	3·41	0·109
35°	41·8	15·4	3·55	4·34	0·104
,,	,,	15·7	3·45	4·55	0·109

Mean value of $k = 0·112$.

0·136 and 0·145. The same instrument was used for the determination of the M values already quoted in Table V, and simultaneous determinations of the ϕ and τ values were made during the exposures over the sulphuric acid solutions used for that purpose. In the case of the three strongest acids, giving atmospheres less than one-fifth saturated, the errors due to the unavoidable exposure of the instrument to the outer air at the start and to other causes bulk too largely for any reliance to be placed on the results, but in 11 tests with more dilute acids k is seen to have a mean value of 0·137, with extreme values of 0·127 and 0·146, and is thus not far from constant and equal to its value in saturated air. These results are shown in the following table:—

Table VII.—Dry Cotton-covered Thermometer ("G") exposed over Water and Sulphuric Acid Solutions at 20° C.

p/P.	p (mm. of mercury).	ϕ (degrees C.).	τ (minutes).	ϕ/τ.	$\phi/p\tau = k$.
0·294	5·1	4·40	6·38	0·69	0·135
0·408	7·1	5·73	6·35	0·90	0·127
0·500	8·7	6·96	6·07	1·15	0·132
0·556	9·7	7·42	5·86	1·27	0·130
0·598	10·4	7·98	5·97	1·34	0·128
0·710	12·4	9·56	5·55	1·72	0·139
0·794	13·8	10·36	5·47	1·89	0·137
0·844	14·7	10·94	5·24	2·09	0·142
0·894	15·5	11·54	5·16	2·24	0·144
0·952	16·6	12·40	5·10	2·43	0·146
0·972	16·9	12·44	5·12	2·43	0·144
1·000	17·4	12·47	5·11	2·44	0·140

The figures in the last horizontal line are the means of those obtained from 11 determinations by exposure over water.

A third series of tests was made with the same instrument ("G") in order to ascertain whether the value of k is different when the dry cotton is exposed in the open air from that already found by exposing it over water or sulphuric acid solutions in the experimental apparatus. For this purpose observations were made on 10 consecutive days (December, 1905) by exposing "G" to the air of the laboratory and taking simultaneous readings of wet and dry bulb thermometers, which were interpreted by Apjohn's formula so as to give the pressure of aqueous vapour. All readings were made by telescope so as to avoid errors which arise from proximity of the observer, and the necessary corrections were applied after comparison of the thermometers with a standard one. The results are shown in the following table:—

Table VIII.—Dry Cotton-covered Thermometer ("G") exposed to the Air of the Laboratory with Simultaneous Wet and Dry Bulb Hygrometry.

Dry bulb.	Wet bulb.	Bar.	p (mm. of mercury).	ϕ (degrees C.).	τ (minutes).	ϕ/τ.	$\phi/p\tau = k$.
17°·23	13°·46	750	9·54	7·43	5·53	1·344	0·141
16·30	12·70	757	9·06	6·80	5·54	1·227	0·135
16·28	13·33	762	9·85	7·50	5·58	1·345	0·136
17·70	14·48	762	10·58	7·86	5·53	1·421	0·134
18·39	15·28	761	11·29	8·26	5·26	1·570	0·139
17·66	14·70	759	10·90	8·06	5·25	1·536	0·141
18·50	14·72	759	10·47	7·56	5·40	1·400	0·134
20·84	16·85	759	12·19	8·19	4·87	1·682	0·138
23·80	18·32	756	12·81	7·61	4·53	1·680	0·131
19·88	15·48	761	10·75	7·30	5·14	1·420	0·132

From these tests it is seen that k varies between 0·131 and 0·141, with a mean value of 0·136, which agrees well with the mean values obtained by exposure over water (0·140) and over varying strengths of sulphuric acid (0·137) in the porous pot of the experimental apparatus.

It follows that such an instrument supplies us with a method of hygrometry which is fairly accurate and easy to use. The method may be worked in the following manner. A suitable thermometer is passed through the bore of a rubber cork, which is fixed in a convenient position on the stem. About a gramme of cotton wool is then wound round the bulb and secured by a few turns of cotton thread. Filter paper may be used instead of cotton wool, and is perhaps more convenient, being less bulky. A desiccator is conveniently constructed by placing a quantity of phosphorus

pentoxide at the bottom of a large wide-mouthed bottle, closed by a rubber stopper through which passes a short glass tube wide enough to admit the thermometer and be closed by its rubber cork. With this arrangement there is no risk of the cotton wool coming into contact with pentoxide. The instrument is always kept in the desiccator except when in actual use, and if observations are taken once in 24 hours the interval is sufficient to ensure dryness. When an observation is to be made, the thermometer is read through a telescope. It is then removed from the desiccator and hung near it, a stop-watch being started at the moment of exposure. The rise of temperature is noted and, as this slows down, a few readings of time and temperature are made at short intervals; and these are repeated as the same temperatures are passed during cooling from the maximum. Two or three points in the neighbourhood of this maximum are sufficient. The thermometer is then replaced in the desiccator, which is left in position for the next observation. The difference between the initial and maximum temperatures gives ϕ. The corresponding time (τ), which cannot be directly observed with sufficient accuracy, is calculated by the rule involved in the equation for the curve, already discussed, that $\tau = (t_1 t_2)^{\frac{1}{2}}$, where t_1 and t_2 are the two observed times at which the same temperature (near to ϕ) is passed. The following example will illustrate the method:—

Temperature.	t_1	t_2	$(t_1 t_2)^{\frac{1}{2}}$.
18°·06	0	0	—
25 ·28	3′ 0″	9′ 7″	5 ·23 mins.
25 ·56	3 23	8 12	5 ·27 „
25 ·84	3 53	7 6	5 ·25 „
26 ·12 (max.).	—		—

Hence $\phi = 26{\cdot}12 - 18{\cdot}06 = 8{\cdot}06$,

and $\tau = 5{\cdot}25$ (mean value).

In order to find the pressure of aqueous vapour in the atmosphere from such observations, the value of k in the equation $p = \phi/k\tau$ must be once for all determined for the particular instrument employed, and this may be done with sufficient accuracy by taking the average result of a few exposures in atmospheres with known values of p,—say over water at known temperatures.

It is not claimed that this method of hygrometry is to be preferred to the usual wet and dry bulb method for ordinary purposes, but it may prove useful in special cases.

Summary of Results.

1. The quantity of hygroscopic moisture required by a given quantity of cotton to put it in true equilibrium with an atmosphere of given humidity, below the saturation value, can be ascertained by taking the mean of the apparent equilibrium values reached by absorption (cotton initially dry) and evaporation (initially over-moist). The progress of either change can be followed by observing the characteristic temperature curve given by a thermometer the bulb of which is covered by the cotton.

2. The vapour tension of any sample of cotton containing a definite quantity of moisture is at different temperatures (at least within ordinary atmospheric range) the same fraction of that of water. The law here is similar to that familiar (Babo's law) in the case of aqueous solutions.

3. Different weights of the same cotton have the same vapour tension when they contain the same percentage weights of hygroscopic moisture. The results are not influenced by tight or loose packing.

4. Filter paper gives results very similar to those obtained with cotton wool; *i.e.*, the same vapour tension corresponds to but slightly different percentage weights of hygroscopic moisture.

5. The vapour-tension curve of moist cotton wool, in which the relative vapour tension (that of water taken as unity) is plotted against percentage weight of hygroscopic moisture, has been determined from $p = 0$ to $p = 0{\cdot}97$ P. Its approach to $p = $ P is probably asymptotic.

6. A new method of hygrometry has been tested, and is described, which is based upon the observations of the rate of rise of temperature of dry cotton when first exposed to moist air.

Postscript.—Since the aforegoing paper was written, we have received the last number of the 'Proceedings of the Royal Society' (No. A 517) containing a paper by Professor Trouton and Miss Pool on "The Vapour Pressure in Equilibrium with Substances holding Varying Amounts of Moisture," which was read at the Society on January 25. As the questions dealt with in the two papers are essentially the same, though the methods employed are different, we may be allowed to state that our experimental work (except the few tests with filter paper recorded in Table IV) was done during 1905 in Melbourne, and in ignorance of the fact that Professor Trouton was similarly engaged.

Trouton's method differs from ours in that he seeks to ascertain the vapour pressure corresponding to a predetermined quantity of moisture, while we have sought to ascertain the amount of hygroscopic moisture which balances

a predetermined vapour pressure. Trouton and Pool have used flannel, which is not a pure material, but in a footnote state that cotton wool has given similar results. Perhaps the most striking of their results is the establishment of the law which has been discussed in the second section of this paper, viz.:—that the ratio of the vapour tension of a hygroscopically moist substance to that of water is independent of the temperature, and of this they give much fuller evidence than we have adduced. In another respect the results obtained by the two methods are in agreement, viz., as to the form of the lower part of the curve for vapour tension and weight of moisture, where a characteristic change of curvature is exhibited. Trouton, however, finds that a parabolic formula fits the upper portion of his curve, pointing to the attainment of the full vapour tension of water itself by material containing only a limited amount of moisture, while our values cannot be so expressed and we incline to doubt the possibility of any such true equilibrium with saturated water-vapour.

No exact quantitative comparison is possible between Trouton and Pool's values and ours because, though they give the weight of the flannel in grammes, they state the quantities of added water in terms of an arbitrary unit, viz., the contents of a capillary tube the dimensions of which are not given. This is all the more disappointing that their paper opens with the statement that "the knowledge of the quantity of water held under varying circumstances by substances of an absorbent character, such as cotton or woollen material, in an atmosphere of any given humidity, is not only of importance in hygrometry, but is also of general interest in connection with the processes used in drying such materials. No investigations, however, of this subject seem, up to the present, to have been ever published." Surely such investigations, when made, lose much of their value when the results are given in terms of units that cannot be interconnected. Perusal of the paper, however, suggests the probable explanation, viz., that Trouton believes that the whole hygroscopic moisture is permanently retained as a surface film, in which case it would be useless to give its actual weight without a correct measure of the exposed surface, which can hardly be obtained. We gather this impression of Trouton's views despite the fact that he himself calls attention, as we have done, to the similarity of the moist material to an aqueous solution in respect to the influence of temperature on vapour tension, and that he specially points out the general similarity between the isothermals for water in flannel and for water in sulphuric acid. The fact should be emphasised, however, that anything more than a very rough agreement between these is not to be expected, even if the moist flannel be regarded as a species of aqueous solution, for the sulphuric acid case is, of

course, greatly complicated by ionisation, the effects of which are for the most part entirely unknown, but are certainly quite different in different parts of the curve. Aqueous solutions of such a substance as glycerine would be much more instructive for comparison, but, so far as we know, there are no data for a complete curve in that or any similar case.

In our opinion the pure surface theory which seems to be held by Trouton is inconsistent with known facts and accepted views concerning the behaviour and functions of cellulose and similar substances; and, unless special evidence be adduced to prove that they are actually impermeable by water, it is only reasonable to assume that the surface film of moisture does (until equilibrium is reached) penetrate and form a species of solution. We hope to offer further evidence on this point later.

In the meantime, the following comparison of Trouton's results for flannel (second series) and ours for cotton shows the extent to which they agree with or differ from one another. The values for the moisture corresponding to the same stated values of p/P have in both cases been read from the curves and, as already explained, are in units that cannot be compared; but it will be seen that the ratios in the last column of the table are fairly constant for middle values of pressure, but diverge at both ends. It seems to us that this divergence at the higher pressures is probably attributable to want of true equilibrium in Trouton's experiments, for our own experience has shown that the attainment of such equilibrium within 12 hours—or even a much longer period—of the admission of water to hygroscopic material is not possible. This error would not interfere with the demonstration of the temperature law given by Trouton and Pool, for we could have based our proof of it on either the absorption or the evaporation tests as well as on the

p/B.	Moisture in flannel in arbitrary units (Trouton).	Moisture in cotton, in percentage (M. and R.).	Trouton's value. / M. and R.'s value.
0·05	1·6	1·16	1·38
0·1	2·8	1·92	1·46
0·2	4·8	3·14	1·53
0·3	6·4	4·14	1·55
0·4	8·0	4·92	1·63
0·5	9·6	5·76	1·67
0·6	11·6	6·80	1·71
0·7	14·0	8·08	1·73
0·8	16·5	9·94	1·66
0·85	18·0	11·3	1·59
0·9	19·6	13·0	1·51
0·95	21·9	15·7	1·40
0·975	23·2	18·0	1·29
1·0	28·0	—	—

mean (true) values; but it would materially affect the other conclusions and especially the statement that the moist material attains to the full vapour tension of pure water when it contains a definite quantity of moisture. Unless very strong and direct evidence were forthcoming, we could not, after our own experience, believe that the whole of each "feed" of water driven over into the space containing the flannel was uniformly distributed as hygroscopic moisture throughout that substance before the vapour pressure was measured, or that no part of the final "feeds" was left as ordinary liquid water to exert its influence.

Calcium as an Absorbent of Gases for the Production of High Vacua and Spectroscopic Research.

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I.—*Introductory.*

This paper contains an account of researches carried out by the aid of an electric furnace designed to heat reagents in soft glass tubes up to temperatures far above the softening point of glass, and has special reference to the use of calcium under these conditions as a valuable absorbent of gases. Recent work on the generation of helium from the radio-elements

has shown the necessity for more simple, certain, and powerful means of absorbing other gases and in particular nitrogen. The usual practice of Sir W. Ramsay and the writer when working together was to make provision for the removal of compounds of hydrogen, oxygen, and carbon, but to take the utmost precautions against the admission of air into the apparatus in the first place. If nitrogen was present in spite of the precautions taken, it was often possible, by gently running the spectrum-tube, to absorb it by the hot electrodes of aluminium, the lines of helium, if present, appearing as the nitrogen spectrum faded.

The difficulty in absorbing nitrogen is that the usual absorbents, for example, a mixture of lime and magnesium, only react above the softening temperature of an exhausted soft glass tube, and the present researches had their origin in an attempt to enable higher temperatures and more powerful absorbents of gases to be used within soft glass apparatus. Lithium, it is true, absorbs nitrogen at a very low temperature, but its use introduces hydrogen. A good example of a very perfect train of absorbents, able to absorb all known gases with the exception of those of the argon family, is to be found in the recent researches of Debierne* on the production of helium from radium and actinium. "Oxygen is absorbed by heated copper; the absorption of hydrogen is secured by the action of heated copper oxide and phosphorus pentoxide, at the same time the copper oxide transforms gaseous carbon compounds into carbon dioxide, which is absorbed by potash, and finally nitrogen is absorbed by pure lithium."

Now such an apparatus serves but one experiment, and has to be built up afresh for each, because it is necessary to fill it after the absorption with mercury in order to compress the helium sufficiently to detect it. The labour involved during a lengthy investigation may be imagined. It is, therefore, very satisfactory to be able to state that I have found that a single reagent, namely, calcium, at the high temperature attainable by the use of my furnace, would serve instead of all the reagents employed by Debierne, and do the work far more effectively and rapidly. Calcium, under the conditions mentioned, is a universal absorbent of all gases with the exception of the argon group.

II.—*Historical.*

Till recently calcium has been a very uncommon metal, while barium and strontium still belong to the category of chemical curiosities. Maquenne† found that when amalgams of these three metals were heated in nitrogen,

* 'Comptes Rendus,' 1905, vol. 141, p. 383.

† 'Comptes Rendus,' 1892, vol. 114, p. 225.

the mercury was volatilised and nitrides of the metals were formed. The absorption took place at a lower temperature than in the case of the metals magnesium and aluminium. Barium was stated to lend itself best to the experiment. None of the alkaline-earth metals were investigated by Lord Rayleigh and Sir W. Ramsay in their examination of the known absorbents of nitrogen,* on account of the difficulties in obtaining large quantities of these metals at that time. After the discovery of argon, Maquenne† showed that a mixture of calcium oxide and magnesium rapidly absorbed the oxygen and nitrogen of the air when heated in a hard glass tube, and attributed this reaction to the production of calcium in an extremely divided state. He states that a manometer attached to the apparatus showed a diminution of pressure from the atmospheric equal to 70 and even 73 cm. of mercury. This mixture is now commonly employed in the preparation of argon, and it is customary to accept Maquenne's explanation of its absorbing power. It is, however, quite certain that the commercial calcium in the form of compact metal bars, produced by electrolysis, behaves in a manner entirely different from the "nascent calcium," if such it be, produced by heating a magnesium and lime mixture, for the former, heated in a tube filled with air at atmospheric pressure, produces no noticeable absorption, even at the highest temperatures.

Moissan first succeeded in preparing calcium in quantity sufficient to make an accurate study of its properties.‡ His calcium was in finely divided crystalline condition, and was obtained by acting upon calcium iodide with excess of sodium. The calcium is deposited out from the sodium on solidification, and the latter is removed by the action of absolute alcohol, which does not attack calcium. He showed that at a dull red heat this calcium absorbs both hydrogen and nitrogen with incandescence, forming nitride and hydride respectively. The hydride heated to the softening temperature of a Bohemian glass tube in an atmosphere of hydrogen neither absorbed nor evolved gas. In a determination of its melting point the calcium was heated in a vacuum obtained by the use of a mercury pump. Moissan noted the evolution of small quantities of gas which were pumped off, "but as soon as the metal became dull red hot the last traces of gas are absorbed, and the vacuum stood at 1 mm." This inconsistency might have been due to sticktion of the mercury in the gauge, or to an error in its reading, for, as Moissan himself remarks, the last traces of gas are absorbed under these conditions.

* 'Phil. Trans.,' A, 1895, vol. 186, p. 187.

† 'Comptes Rendus,' 1895, vol. 121, p. 1147.

‡ 'Comptes Rendus,' 1898, vol. 126, p. 1757, and vol. 127, pp. 29, 497, and 584.

Calcium, electrolytically produced in the form of compact bars, free from mercury and oil, has been available for over two years, and has been the subject of much interest. Those who have examined it must have been more struck with its apparent disinclination to react than with any exceptional reactivity. Thus the attempts to replace the magnesium or magnesium-lime mixture by this calcium in the preparation of argon have never succeeded in my experience. Even when heated to 1200° C. in an electric oven it refuses, after a very slight initial action, to absorb nitrogen. It must be heated to a very high temperature in the blow-pipe before it ignites in the air, and then readily goes out. In one experiment a powerful arc was caused to pass between calcium points in air without inducing combustion.* Negative results of this character could be multiplied.

Arndt† undertook a research on the melting point of commercial calcium, in which the metal was heated, as in Moissan's experiment, in a vacuum of 1 mm. pressure to avoid chemical action. He noticed that the calcium began to volatilise below its melting point, and that the vapour reacted energetically with the residual air, so that the pressure on the manometer sank to an unreadable value. Absorption commenced at 700° C., was rapid and accompanied by visible volatilisation at 730°, whereas the melting point was found to be 800°. When a Plücker spectrum-tube was included, it was found that "the nitrogen spectrum faded rapidly, while the lines of hydrogen (from a trace of water present) remained behind with the lines of argon." He found that the vapour of magnesium did not exhibit nearly the absorptive power of calcium.

With the use of the apparatus to be described I arrived independently at, and have confirmed, the observation of Arndt on the extreme rapidity of absorption of the oxygen and nitrogen of air by the vapour of calcium. In addition I have found that all the common gases can be absorbed equally well, although in some cases, as the above quotation from Arndt's paper shows for hydrogen, complete absorption is not effected by simple heating alone.

III.—*Electric Furnace for Strongly Heating Reagents in Glass Vessels.*

The apparatus usually employed depends upon the internal heating of the reagent by an electric resistance circuit and the protection of the glass walls

* This, however, is partly due to the extraordinarily slight heating which electrodes of calcium experience when a discharge is passed through a gas between them. Of all metals calcium heats the least, and is in this respect far superior to aluminium. But for other difficulties it might be used to replace aluminium, with advantage, as the electrods of vacuum tubes in the case of the inert gases. A steady arc can be maintained between calcium points in air with a very small ampèrage.

† 'Ber. d. D. Chem. Ges.,' 1904, vol. 37, p. 4733.

by a screen of porcelain placed between it and the enclosed furnace. It is shown to the scale of 6 inches to the foot, in section, in fig. 1. Figs. 2, 3, 4 are transverse sections on the lines x, y, z respectively. The outer containing

Fig. 1.

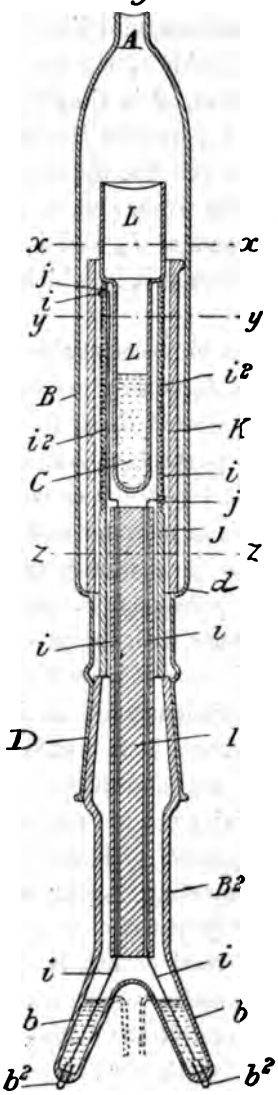

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Fig. 2

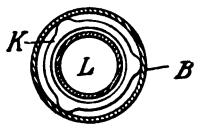


Fig. 3.

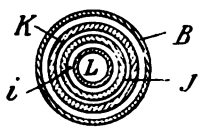


Fig. 4.

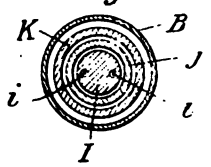
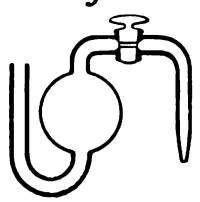


Fig. 5.



vessel is made out of soft glass tubing, and is in two parts, the upper B and the lower B_2, which are ground to fit together accurately at D. The lower part B_2 has two mercury cups with platinum wires b_2 sealed through the glass. The upper part B widens at the shoulder d, on which rests the

porcelain shield-tube *K*. This is slipped into the tube, which is then constricted at *A* and joined to a narrow piece of tubing for connecting to other apparatus. The furnace-tube *J*, which carries the heating wire, slides through the ground-joint of *B* and passes inside the shield-tube *K*. For the upper part of its length it is grooved with an external screw thread of about 1 mm. pitch, and wound with a platinum wire *ii* of 0·25 mm. diameter. It passes through the holes *jj* into the inside of the tube, and is joined to stouter leads of nickel, copper, or platinum, or is simply doubled on itself. The leads pass through the doubly-bored porcelain insulator *I*, which slips within the lower half of the furnace tube and the upper part of B_2, and are finally taken into the mercury cups. The lower end of the furnace-tube *J* rests on, and is supported by, the upper end of B_2, and itself surrounds and supports at its upper end a porcelain test-tube *L*, in which the reagent to be heated is placed, at *C*.

The whole arrangement is readily taken to pieces at the ground-joint *D* for recharging, cleaning, or repairs. The end B_2 usually carries between the two mercury cups a narrow tube, shown by dotted lines, to which is attached a bulb and tap, shown in fig. 5, for the purpose of admitting mercury into the apparatus without introducing air, and also for conveniently filling the mercury cups and other purposes. An oil or mercury seal may surround the ground-joint, but is not necessary if it is of good workmanship.

For special work, where the possibility of leaks or the presence of vapour of grease is to be avoided, it is easy to dispense with the ground-joint *D* and to make the apparatus in one piece. In this case *B* is made long, so that it can be repeatedly opened and sealed, and the various parts are introduced through the upper end by suitable tongs. But these refinements are usually quite unnecessary if the ground-joint is of good workmanship, and is well lubricated, and if the leads are of sufficient conductivity not to heat the joint. In special work, too, the mercury cups may be dispensed with and the wires continued through the glass seal if the presence of mercury vapour is to be avoided.

[*Added.*—An improved and thoroughly satisfactory method of working, applicable whether the ground-joint is used or not, is to dispense with the porcelain insulator *I*, and to bore two holes opposite each other at the lower end of the furnace-tube *J*, twisting one end of the doubled platinum heating wire through each hole, together with a length of "flexible" copper wire, and continuing the two flexibles, insulated if necessary in little glass tubes, into the cups *bb*, where they make good touching contact with the platinum, without the use of mercury. In this way a mechanically strong joint with the fine heating wire is secured, the presence of mercury inside the vacuum is altogether avoided, and the formation prevented of a mercury arc between

the two cups when a high-tension discharge is passed through the vacuum, which in the first form of apparatus constituted an occasional source of annoyance and damage.]

With this apparatus reagents may be safely heated to temperatures far above the melting point of glass without injuring the apparatus. After nearly two years' use of these furnaces I do not recall a single case where the heat has caused the glass to crack or break while in use, although, of course, the glass tends to get brittle and to break when being cleaned more readily after use than before. If required for prolonged heating at high temperature, it is an advantage to blow a bulb on the tube at the hottest part of the furnace, otherwise, when the porcelain shield-tube has become heated through, the glass is apt to melt. These shield-tubes never break. The furnace-tubes are more fragile, but stand extremely well, while, of course, the test-tubes containing the reagents require the most frequent replacement. Tubes made of thin iron would for many purposes have very many advantages over porcelain. But they must be gas-tight at the lower end, for the vapour of calcium would ruin the platinum wire if it came in contact with it.

The limit of temperature attainable in this apparatus is fixed mainly by the volatility of the heating wire in the high vacuum usually maintained within the apparatus, and for this reason platinum or one of its alloys must be used. Iron or nickel volatilise and the wire is destroyed in a few minutes. Even with platinum the volatilisation of the metal is serious at a bright-red heat. In addition, a certain tendency to become brittle with loss of metallic qualities, which is noticeable in ordinary platinum resistance furnaces, thermometers, and thermocouples, and which prevents their prolonged use at temperatures above 1200° C., appears to be far more marked and to take place at lower temperatures in the high vacuum, rendering occasional rewindings of the furnace necessary. The cause of this has not been fully explained. An examination of somewhat analogous phenomena in the case of nickel has been recently made by Dr. H. C. H. Carpenter in a paper read before Section G of the British Association this year, and attributed by him to gases in the nickel.* I am inclined to connect the phenomenon in the case of platinum with the vaporisation of the metal. If tantalum wire could be obtained, no doubt it would prove far more suitable than platinum. Naturally, a high vacuum within the apparatus tends greatly to conserve the heat and to diminish convection, and the risk of the outer vessel melting. In this respect the apparatus is the antithesis of the Dewar vessel for storing liquid air.

* 'Engineering,' August 17, 1906, p. 222.

IV.—*Absorption of Gases by Calcium.*

If the apparatus described, charged with a small piece of calcium, and furnished with a Plücker spectrum-tube, is exhausted by a Fleuss pump, and the furnace heated, gases, consisting of compounds of hydrogen, carbon, and oxygen are given out by the calcium. If connection with the pump is then shut off and the heating continued, absorption of the remaining gases, accompanied by volatilisation of the calcium, takes place, and the vacuum rises almost instantly to a point at which no discharge can be passed through the spectrum-tube. By a non-conducting vacuum is to be understood one of greater resistance than an alternative spark gap in air of 2 to 3 cm., unless the length of the gap is given.

If air is introduced into the apparatus, all but argon is rapidly absorbed, and quantities up to 10 or 20 c.c. can be thus dealt with. These experiments with air are, however, of interest from so many points of view that they will be dealt with in detail later.

In a similar way it was shown that carbon monoxide, carbon dioxide, water vapour, hydrogen, acetylene, sulphur dioxide, ammonia, and the oxides of nitrogen (nitric oxide, with deflagration of the calcium) are all as readily and completely absorbed as in the case of the oxygen and nitrogen of the air. Quantities of several cubic centimetres disappear within a minute after introduction, and the vacuum-tube becomes non-conducting.

Finally, in order to put the power of the calcium to as severe a test as possible, several successive quantities of coal gas, each of several cubic centimetres, were introduced into the apparatus after the absorption temperature had been attained. Within a minute after each addition the spectrum-tube became non-conducting to the discharge. Calcium thus acts as a universal absorber of chemically valent gases.

The case of hydrogen and its compounds alone calls for fuller treatment, for at too high temperature calcium hydride possesses an appreciable tension of dissociation. The same is of course true of calcium carbonate, but this compound does not appear to be formed when only small amounts of carbon dioxide are absorbed by the calcium. If hydrogen or its compounds are present in a gas in large quantity, the spectrum-tube, after the absorption of the other gases, shows still the hydrogen lines, and refuses to become non-conducting as long as the temperature of the furnace is maintained. But if the heat is reduced, the non-conducting stage is reached at once. In one experiment 1 c.c. of hydrogen was introduced, and the heat reduced. The spectrum-tube became non-conducting in 40 seconds.

Careful experiments have shown that even after cooling an infinitesimal

quantity of hydrogen remains unabsorbed. Thus if, after cooling, mercury is allowed to fill the apparatus and compress the residual gas many hundred times into a tiny spectrum-tube, a very faint hydrogen spectrum can be seen, although the spectrum-tube, even after this concentration of the gas, is still of high resistance and fluoresces brilliantly under the discharge. This residual trace will be shown to be of great value in certain experiments.

A point of very great practical importance arises out of the dissociation phenomena of calcium hydride. Different commercial specimens of electrolytic calcium exhibit differences in their behaviour which I have traced to the presence of hydride in some specimens and not in others. The presence of this hydride quite alters the characteristics of the absorption process, and although with sufficient experience it is possible to get good results in spite of the presence of hydride, this experience is apt to be dearly bought. When hydrogen is present the real absorption temperature is apt to be overstepped, for instead of a non-conducting vacuum being obtained, as it should be almost instantly with a proper specimen of metal, the dissociation tension of the hydrogen is sufficient to enable the discharge to pass. An inexperienced operator, or one accustomed only to the character of the purer metal, will, in consequence, continually increase the temperature, and the tension of the hydrogen of course increases, and may ultimately become quite measurable on a gauge. Before it is realised that the proper temperature has been far overstepped, the metal may have melted, subsequently to crack the crucible on cooling, the platinum wire may fuse or volatilise, and even the glass envelope may soften. Whereas, if instead of increasing the temperature the heat had been cut off, the non-conducting stage would have been reached in a few seconds. It was noticeable that of two specimens, one excellent and the other containing hydrogen and unsuitable, the latter was by far the more malleable and could be always detected by this test after it had accidentally got mixed with the other specimen. But this difference of properties may not have been due to the presence of the hydride. No one would use metal containing hydride wittingly, but it is well to know that by cutting off the heat, when the spectrum of the gas becomes that of hydrogen, quite satisfactory results are attainable. But the sacrifice of time and apparatus, destroyed by excessive temperature, was considerable before the differences between the specimens of metal were suspected, and the differences of behaviour understood.

Experiments were tried to see if calcium which had been strongly heated and allowed to cool in an atmosphere of helium and argon, respectively, re-evolved any trace of these gases when reheated *in vacuo*, but in each case with negative results.

V.—*Behaviour of Barium and Strontium.*

Tested under the same conditions, barium and strontium show very analogous behaviour to calcium. The specimen of barium employed had been preserved under oil, and was in the form of a granular powder. It had been prepared from the amalgam and still contained mercury. It was given a preliminary heating *in vacuo* to remove oil and some of the mercury. It commenced to absorb gases without appreciable volatilisation at a temperature notably below that required in the case of calcium. A non-conducting vacuum was usually not obtained before the metal had been allowed to cool. In the work with both barium and strontium the hydrocarbon spectrum, reminiscent of the argon gases, was very frequently observed, and was probably due to traces of the oil in which the metals had been preserved. This spectrum usually appeared when the metal was hot, and disappeared on lowering the temperature, the vacuum becoming non-conducting. Coal gas was admitted to the heated barium to a pressure of 2 to 3 mm., and was rapidly absorbed, and a non-conducting vacuum obtained without difficulty. Air introduced to about 7 mm. pressure was rapidly absorbed, except for argon, exactly as with calcium.

Barium *can* be heated to its absorbing temperature in a hard glass tube by a Bunsen burner, but the tube collapses and cracks on cooling. Under similar circumstances calcium requires a blowpipe to induce volatilisation and absorption, and the tube is completely melted and flows round the calcium in the process.

Experiments with strontium were less complete on account of the difficulty of obtaining the real metal, and on account of the small quantities that had to be used. The first sample bought as strontium proved to be potassium amalgam simply, without sufficient strontium to give a precipitate with sulphuric acid. The metal, when it was obtained, proved to be similar in properties to barium and calcium. On account of the cost only a decigramme at a time could be used, and it is very probable that its behaviour, as observed, was partly due to presence of alkali metals, oil, and mercury, and that electrolytic strontium in compact form, free from these contaminations, would exhibit a behaviour even more nearly allied to calcium. So far it has not been possible to procure this. Absorption with the sample employed seemed to start at a slightly higher temperature than with calcium, and at a high temperature some volatilisation of the metal appeared to occur. This was due probably to a trace of alkali metal. It showed to a very marked extent the phenomenon of not giving a good vacuum until it had been cooled down, and of showing hydrocarbon spectra very strongly, but this behaviour might

not be shown by an oil-free specimen. It seemed hardly worth while to pursue experiments with a metal at once so costly and so impure, when a commercial process has been patented for producing the metal on a scale similar to that of calcium. But the experiments proved that, like barium and calcium, it can absorb coal gas and air, and give a non-conducting vacuum without difficulty.

VI.—*Production of High Vacua by Means of Calcium.*

From what has been said it will be seen that the apparatus described affords a ready means of obtaining a high vacuum by the use of calcium as an absorbent. Arndt, in the paper referred to, suggested its use in the production of high vacua, on account of the energetic action of the vapour on the residual air. A little consideration, however, shows that since argon is not absorbed by the reagent, air must be as rigorously as possible excluded. As is well known, the real difficulty in the production of high vacua depends not so much on the removal of all the original air, which is comparatively easily and quickly accomplished even with a pump, but on the effective removal of the gases which are condensed on the glass walls of the vessel being exhausted, and which tend to recondense in the pump when driven out of the vessel, and to introduce a kind of steady vapour pressure until they have all been removed. The value of calcium as a means of producing the highest vacua depends on its power to absorb almost instantly the gases condensed on the glass walls as soon as the latter are expelled by heating. It is, as stated, necessary to replace all the air in the apparatus before the absorption with calcium takes place, or the residual argon will prevent the vacuum obtained from being really good. The importance of this is increased by the fact that articles for exhaustion have usually to be provided with a very constricted orifice, so that they can be sealed safely after the vacuum has been obtained. As a consequence, any argon accumulating in the absorption chamber dams back the flow of absorbable gas from the vessel being exhausted, and enormously increases the time required, as the contents of the vessels have to diffuse and mix through the constricted orifice, and this process may require some minutes. Hence, in this method of high vacua production, the customary precautions must be taken against the leakage of air, if really high vacua, as distinguished from the apparently high vacua later to be considered, are desired.

If a Fleuss pump in good order is available, and new glass apparatus which has not before been exhausted is being dealt with, it suffices to continue the pumping while the apparatus in question is heated in the usual way to expel condensed gases, and so utilise the latter to replace the residual

air remaining in the apparatus. Or, if a new charge of calcium, not previously heated in a vacuum, is employed, the same displacement of the air can be readily effected by the gases given out by the calcium before it attains its absorption temperature. In both cases the gases consist chiefly of carbon and hydrogen compounds and, being free from argon, serve well for the displacemement of the remaining air. In other cases, or where more certainty is desirable, the complete replacement of the air may be effected by the use of a side tube containing a mixture of potassium chlorate and manganese dioxide, which evolves oxygen on warming. One or two small quantities of oxygen are admitted during the pumping, and the connection with the pump closed or sealed off before the calcium is brought into action.

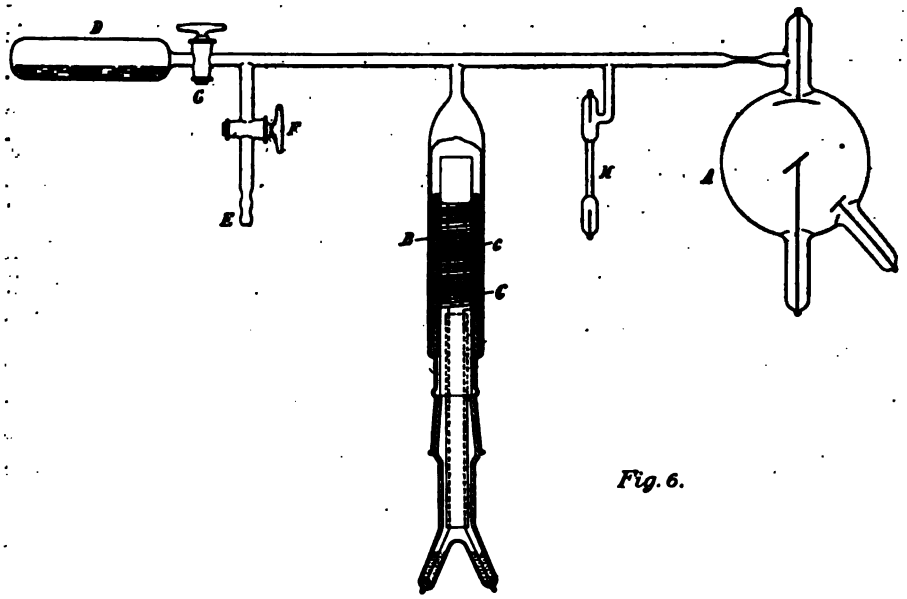


Fig. 6.

Fig. 6 shows, in diagram, an apparatus suited for the purpose of exhausting an X-ray bulb. *C* is the calcium heated by the platinum wire *c* within the glass vessel *B*. *A* is an X-ray tube, and *D* is a tube containing the oxygen mixture. The Fleuss pump is connected with *E*, and the spectrum-tube *H* is a convenience both for judging of the degree of vacuum and the character of the residual gas.

With this method, as in all methods of vacua production, the degree of rarefaction attained is the balance between the rate of absorption or removal of the gas present, and the rate of supply of fresh gas from leaks or from condensed films, or from substances such as lubricating grease or mercury which have a vapour pressure. Since the rate of absorption

is extremely rapid, good results can be obtained even under poor conditions. Conditions have to be very bad indeed for any difficulty to be experienced in the production of a so-called "X-ray" or "non-conducting" vacuum. But it will be shown in the sequel that these electric discharge phenomena may be produced in vacua which could not be described as high in any other sense. With proper care the very highest vacua may be obtained by the use of calcium, as is proved by the experiment quoted in Section IV, of filling the apparatus with mercury and compressing the gaseous contents several hundred times. Personally, in crucial experiments, I should use it preferably to any other, and in the research on the positive charge carried by the α-particle* it was the final court of appeal, by which results obtained by other methods were always retried.

VII.—*An Induction Method of Electrically Heating Calcium in Glass Vessels.*

Calcium is an excellent conductor of electricity, being the fifth best if wires of equal length and diameter (Ag, Cu, Au, Al, Ca), and the third best if wires of equal length and weight (Na, Li, Ca, Mg, K, Al) are compared. Its volatility, relatively low melting point and low resistance are all against the possibility of heating calcium to its absorbing temperature by conducting a current through it. But in the form of fairly massive discs or rings calcium may be heated to its melting point by induction through the glass walls of the containing vessel by means of alternating circuits outside the vessel. For instance, if a bundle of iron wires, similar to the core of an induction coil, is put through a ring turned out of a bar of calcium, and the whole placed in an exhausted glass tube, the walls of which are protected from fusion by a porcelain shield-tube in the manner before described, and a bobbin of insulated wire traversed by an alternating current of high periodicity be slipped over the glass tube, the calcium may be readily heated to its absorption and volatilisation temperature. The arrangement is simply a step-down transformer, in which the calcium ring acts as the single short-circuited winding of the secondary, and, being of low resistance, a fraction of a volt induced in it by the magnetic flux suffices to cause the passage of a heavy current, probably of the order of a kilo-ampère, which heats it to the required high temperature. Fig. 7 shows one arrangement for this purpose.

Fig. 8 is a transverse section on the line *ww*. The iron core *M* is enclosed in a thin tube of Jena glass *P*, which is exhausted and sealed. This tube effects the double purpose of protecting the iron from excessive heat and retaining gases given off from the iron, but can be dispensed with. *C* is the

* 'Nature,' August 2, 1906, p. 316.

calcium ring, *K* is the porcelain shield-tube, *B* is the outer glass containing tube, *N* is the external circuit through which the inducing current is passed. As the heat given out from the calcium is considerable and apt to injure insulating material, it is convenient to employ, instead of a bobbin of insulated wire of many turns, a few turns of stout, bare, copper bar or tube, and to obtain the inducing current from the secondary of a step-down transformer not shown in the drawing. Since the magnetic flux, and therefore the inducing voltage in *C*, varies as the square of the diameter of the core, while the resistance of *C* varies as the diameter, it follows that the larger the diameter of cross-section of the apparatus the easier it is to obtain the desired result. But the induced voltage depends also on the periodicity of the inducing current, so that the latter must be the higher the smaller the apparatus employed. The dynamo employed was specially constructed for the purpose and gave with variation of speed a periodicity from 200 to 400 cycles per second. The drawing shows the apparatus to the scale of 6 inches to the foot.

Fig. 7.

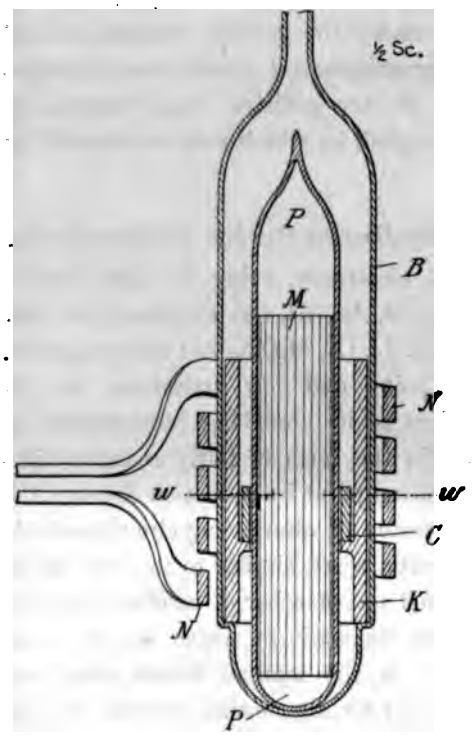
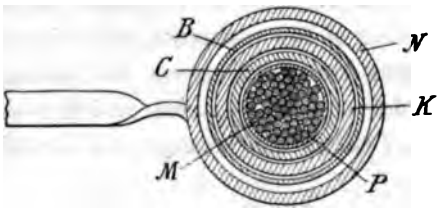


Fig. 8.



Another form of apparatus is shown in fig. 9, to the scale of 3 inches to the foot. It differs from the last mainly in that the magnetic circuit, composed of the iron strips or wires M_2 *M M* M_2, is closed but for the two air gaps where the glass walls of the containing vessel penetrate it. The use of the step-down transformer is unnecessary, because the inducing bobbins, represented diagrammatically by the circuit *N N N N*, are far enough removed from the source of heat not to be damaged.

Fig. 9.

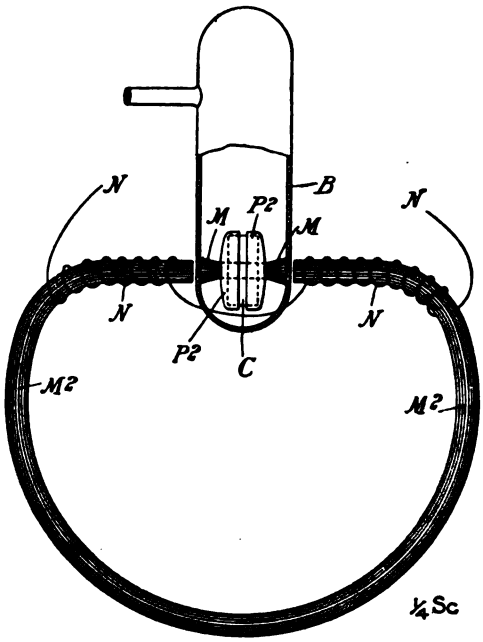


Fig. 10.

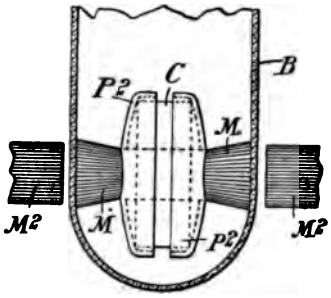


Fig. 12.

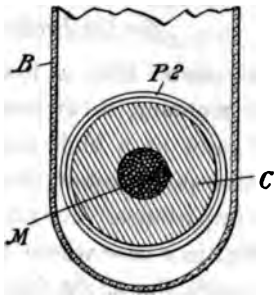


Fig. 11.

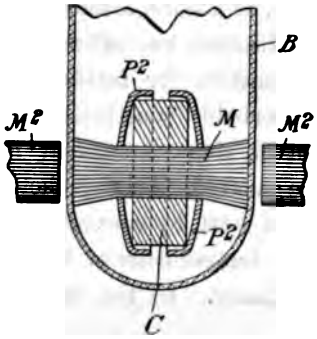
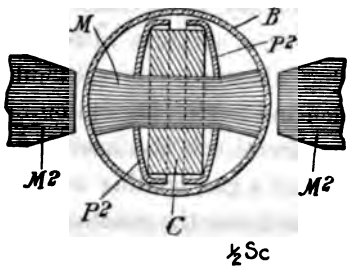


Fig. 13.



The part within the glass containing vessel is shown to twice the scale (6 inches to the foot) in fig. 10. Fig. 11 is a section of the same. Figs. 12 and 13 are transverse sections in vertical and horizontal planes respectively. *C* is a disc of calcium bored with a central hole, through which passes the bundle of iron wires *M M*. P_2 P_2 are two porcelain crucible lids bored with central holes. Instead of the disc of calcium shown, a disc one-third the thickness between two similar discs of copper may be employed if it is required to increase the conductivity. Since in these induction methods of heating the heat is developed in the reagent itself, the latter is hotter than its surroundings, which is a great advantage, as far less screening of the glass walls suffices. The temperature of the metal can be very accurately judged by the eye, and must be kept below the melting point. A moderate red-heat just above the cherry-red stage is necessary for absorption of gases and volatilisation to occur.

For experimental work where cost is not the primary consideration, and where frequent dismantling of the apparatus is rendered necessary, the resistance-furnace method of heating is to be preferred. But for prolonged work in which the object is simply to obtain a high vacuum, the induction method offers great advantages.

VIII.—*Some Practical Considerations in the Use of Calcium as an Absorbent for the Production of High Vacua.*

There is no doubt that a low initial pressure, not exceeding a few millimetres of mercury, is as essential a condition in causing calcium to combine with gases as a high temperature. As Arndt showed, there is a slight initial absorption below the volatilisation temperature, and this is of great practical importance. For rapid and continuous absorption volatilisation is essential. But in a case where the initial pressure is above that at which volatilisation occurs the slight initial action is often sufficient to lower the pressure to the extent necessary for the formation of vapour. When this has once taken place subsequent absorption is much facilitated, for the film of volatilised metal continues, even in the cold, to absorb, although more slowly than the vapour itself. Hence once volatilisation has taken place there is present a tendency to re-establish the condition for further vaporisation. When, however, a mixture with an unabsorbable constituent, for example, air, is being absorbed, the accumulation of this constituent hinders the volatilisation and further absorption by the calcium. Another factor operating in the same direction is the increased loss of heat by convection currents in the presence of a gas, tending to lower the temperature of the reagent and furnace, and to lower the resistance of the latter. In the usual case, where

this resistance is small compared to the external resistance in the circuit, the fraction of the electrical energy dissipated within the furnace is also lowered, and so the temperature falls from a double cause. If water vapour is present the action becomes extremely marked on account of the great conductivity of this vapour to heat. The current necessary to raise the temperature in this case may be so great that, unless promptly reduced when absorption commences, the heating circuit is apt to be destroyed.

Under proper conditions of working the calcium should never be melted, although it may be volatilised completely and redeposited on the cooler part of the tube as a compact tube or ring difficult to remove by mechanical means. Used porcelain tubes should never be exposed to the air or treated with water or dilute acids, as they readily crack under this treatment. Immersion in concentrated hydrochloric acid usually serves to dissolve the volatilised metal without cracking the tube, but with the liberation of the spontaneously inflammable silicon hydride. If the calcium is melted in the tube the latter usually cracks on cooling, so that for many reasons suitable iron tubes would be better than porcelain. The narrow margin of temperature, 70° C. according to Arndt, between the volatilisation and melting point need, however, never be exceeded when experience has been gained and suitable metal is employed. The presence of hydride in the metal acts so prejudicially largely because the dissociation tension of hydrogen lessens the volatilisation and reduces still further this narrow margin, so that the melting point is the more likely to be overstepped. These conclusions as to the conditions under which calcium should be employed as an absorbent have been arrived at after over a year's continuous use of the method.

The following experiment on the effect of vapour of grease and of a very constricted orifice between the vessel being exhausted and the absorption chamber is instructive. An X-ray bulb was connected to the calcium absorption apparatus provided with a ground-joint. The latter was lubricated by the well-known mixture of rubber, paraffin-wax and vaseline, employed by Sir W. Ramsay. A spectrum-tube was provided and the apparatus exhausted by the Fleuss pump, and the connection with the latter sealed off. The calcium was brought into action and a vacuum corresponding to an alternative spark-gap of 15 cm. obtained in the X-ray tube. It was then left over night in connection with the furnace, so that the vapour from the grease of the ground-joint could exert its full effect. In the morning the vacuum was so low that there was no trace of green fluorescence in the tube. The calcium was heated and allowed to cool. In 40 minutes the 15-cm. alternative spark-gap was again attained.

Then, hour by hour, the vacuum slowly deteriorated till the alternative

spark-gap was *nil* and the green fluorescence disappeared. This process of heating the calcium and leaving till the vacuum went right down was repeated day by day for a week. It was noticed that it always took 40 minutes after heating the calcium before the 15-cm. spark-gap was regained, and this period represented, as numerous experiments with the same tube show, the time taken by the gases to flow out of the X-ray bulb through the constricted orifice when a practically perfect vacuum existed on the other side. It happened that the constriction was unusually and unnecessarily narrow, such as an amateur not realising the importance of it would make, but the necessity of this constriction, where the tube is ultimately to be sealed off, imposes a natural limit on the time taken for the exhaustion, however rapid a method of absorption is employed. In this experiment the spectrum in the Plücker tube, when the vacuum was low, was due to hydrocarbons, and nitrogen was never seen. That there was no appreciable leak of air was also shown by the fact that even at the end of a week no lines of argon could be seen. This shows that the deterioration of the vacuum was simply due to vapour being slowly given off from the grease used for lubrication. A properly constructed ground-joint is wonderfully air-tight. I may mention that in 1904 I constructed one of Strutt's so-called radium clocks with a ground-joint similar to those employed in the furnaces. The period of the clock is the same now as when constructed, and it has worked continuously without re-exhaustion, proving conclusively that no trace of air has leaked through the ground-joint. Hence, in the calcium method, where the vapours of lubricants are absorbed with rapidity, as many taps, ground-joints and similar conveniences as desired may be employed without harm, provided they are well lubricated and never get heated, and that the apparatus being exhausted is sealed off as soon as the high vacuum is attained.

IX.—*Quantity of Argon Detectable by the Spectroscope.*

If air is admitted to heated calcium the oxygen and nitrogen are absorbed almost instantly, and the argon and its companions in the atmosphere remain behind in a state of great purity and freedom from ordinary polyatomic gases. In the apparatus used an arrangement of two taps for admitting known small quantities of gas was joined to the apparatus for the absorption of gases by calcium. The space between the taps was 0·13 c.c. and the total volume of the apparatus was 123 c.c. The partial pressure of argon is 0·0094 of the atmospheric, or 7·1 mm. Each quantity or "dose" therefore of 0·13 c.c. of air admitted to the apparatus corresponds to a pressure of argon of 0·0075 mm. of mercury. The vacuum-tube employed was an ordinary Plücker tube, with aluminium electrodes, of about 4·5 c.c. capacity. It was found that no trace

of the argon spectrum could be seen in the tube, and no discharge would pass through until three doses of air had been admitted and absorbed. At this stage the group of greens and the orange line in the spectrum were faintly visible. With four doses the red lines were visible momentarily as the nitrogen spectrum faded, and with five doses these became permanent. After 10 doses (1·3 c.c.) of air had been introduced, the whole argon spectrum was brilliant; 4·5 c.c. were so added in small quantities and then 3 c.c. at once. In one minute the nitrogen spectrum began to clear and 1·5 minutes the argon reds were visible. In two minutes nitrogen had disappeared, and in under three minutes only argon and hydrogen were visible. The hydrogen disappeared when the heat of the furnace was reduced and the tube, giving a perfect argon spectrum, was sealed off as a memento of the experiment.

In another experiment the volume of the apparatus was 100 c.c., and 12 c.c. of air were admitted in one quantity after the calcium had been heated *in vacuo* to the absorbing temperature. This was absorbed without difficulty. The residual argon must have exerted about 1 mm. pressure. Yet the spectrum-tube showed brilliant green fluorescence. A tap was opened and the argon allowed to flow into a similar volume of 100 c.c. which had previously been perfectly exhausted. The pressure was thus reduced to about 0·5 mm., and at this stage the spectrum-tube had a resistance equivalent to an alternative spark-gap of 5 mm.

It follows from these experiments that below a pressure of 1/50 of a millimetre no discharge can be sent through a tube containing argon. At this pressure the greens and orange become faintly visible, and at 1/25 of a millimetre the reds appear. At 0·5 mm. the resistance of the tube is still so high that the discharge prefers to jump an air-gap 5 mm. long, while at a pressure of 1 mm. the tube is brightly fluorescent.

It was found that the substitution for the ordinary vacuum-tube of one of minimal volume with platinum electrodes did not much affect the pressure of gas at which the spectrum became visible. With a tube of 0·3 c.c. volume, which is as small as it is convenient to employ, a quantity of argon less than 1/100 of a cubic millimetre, measured at normal temperature and pressure, could not be detected by the spectroscope. This applies to the pure gas in the absence of almost every trace of the relatively far more conducting polyatomic gases. As in the case of helium, to be considered, smaller quantities of argon could be detected in presence of hydrogen or other polyatomic gas.

X.—*Misapprehensions Regarding High Vacua.*

The foregoing experiments with argon, and others of a similar character with other monatomic gases, serve to show that the characteristics of the

electric discharge may prove a very faulty guide to the degree of a vacuum. The terms "X-ray vacuum," "fluorescent vacuum," etc., afford, apart from the knowledge of the character of the residual gas, no indication at all of the actual pressure. For if it happens that the residual gas is a pure monatomic gas, the fluorescent stage and even the non-conducting stage are reached at pressures within the range of the mercury barometer. These considerations serve to connect numerous isolated facts familiar to those who have worked with high vacua. Thus it is well known that to pump out a spectrum-tube with a mercury pump takes far less time if the gas pumped out is argon or helium than if air or hydrogen has been present.

[*Added.*—It is also well known* that in vacuum-tubes filled with inert gases great heating of the electrodes occurs, even when these are made of aluminium, accompanied with the rapid disentegration of the electrode and the volatilisation of the aluminium. At the same time a rapid exhaustion of the supply of gas apparently takes place, the vacuum appears to rise, the tube rapidly becomes fluorescent with use, and the resistance increases to the non-conducting point at which no discharge can be passed through the tube. In the past this has been attributed to the absorption of the gas by the electrodes and the walls on which the volatilised aluminium is deposited. The advantages of aluminium over other metals, such as platinum, have been ascribed to a more rapid absorption in the case of the heavier metals.† Attempts to recover the gas supposed to be absorbed, by heating the apparatus, solution of the metal electrodes, etc., have not been successful, as only a trace of the gas is recovered in this way.

The true explanation of the phenomenon is quite different, and follows simply from the experiments given in section IX for argon, and similar ones in sections XI and XII for helium. The inert gases are not absorbed, but remain in undiminished quantity in the gaseous state in the tube, but the traces of ordinary chemically active gases always present, initially or introduced from the electrodes during the discharge, are absorbed, and the tube becomes in consequence non-conducting. The experiments of Skinner have an important bearing on this question, and in his most recent paper‡ he summarises his conclusions. When a current is passed through a vacuum-tube, entirely independently of the nature or amount of gas filling the tube, hydrogen is evolved from the cathode and absorbed by the anode at a rate initially equal to that required by Faraday's law. Aluminium and magnesium cathodes give out hydrogen much more freely than the denser

* Compare, for example, E. C. C. Baly, 'Phil. Trans.,' A, 1903, vol. 202, p. 183.

† Compare Travers, 'Study of Gases,' p. 299.

‡ 'Phil. Mag.,' November, 1906, p. 481.

metals, but the rate of *evolution* from the cathode rapidly falls off as the supply of gas in the surface layers of the metal is exhausted. If the tube is allowed a rest the initial rate is recovered. When a continuous discharge is passed through any tube, therefore, the vacuum improves, for the rate of absorption by the anode gains on the rate of evolution from the cathode, and this should suffice to explain the well-known improvement with use in the vacuum of an X-ray tube. According to Skinner, helium and argon are *not* absorbed by the electrodes, hence the rapid exhaustion or "running out" of the tube and the advantages of the aluminium electrode are to be explained only in the manner indicated. It is intended to try, by passing a unidirectional current through a tube filled with inert gas, to what gas pressure the non-conducting stage can be pushed. It is not a little remarkable from the theoretical point of view that helium, which conducts so much more readily than any other gas under usual conditions at high pressure, should exhibit the peculiar behaviour it does at low pressure in a state of purity.

Frequently in the work on the production of helium from radium, in conjunction with Sir William Ramsay, it was noticed when "running" a spectrum-tube to absorb nitrogen and reveal helium, if present, that, although a severe and prolonged running might be necessary to absorb the nitrogen, it always "ran out" first, and helium, however minute in quantity, showed itself, if present, as the nitrogen spectrum faded. When, however, the nitrogen spectrum had completely faded, which it did usually with great rapidity once it commenced to weaken visibly, the helium "ran out" almost instantly, if only in minute quantity, and the tube refused to conduct the discharge. This sharp preferential absorption, as it seemed, of the nitrogen first by the electrodes, so that, even after a quarter of an hour's hard running, the helium would survive, instantly to disappear as soon as the nitrogen faded, always seemed to me almost providential, until, recently, the true explanation became obvious.]

The explanation is also to hand why the presence of mercury vapour affects the action of the mercury pump so little. The vapour pressure of mercury at room temperature is between 1/500 and 1/1000 of a millimetre. In the case of hydrogen or carbon dioxide it is probable that this pressure would be sufficient to conduct the discharge and prevent the vacuum appearing very high to the electrical test. That "high vacua" can be obtained at all by the mercury pump is probably due to the fact that mercury vapour is monatomic.

Similar considerations apply to the vacua so readily and simply obtained by the use of charcoal cooled in liquid air according to the method now largely used in scientific investigation and first employed by Sir James Dewar.* It

* 'Roy. Soc. Proc.' A, 1904, vol. 74, pp. 122—131.

happens here also, as in the case of the calcium method, that the unabsorbed gases are monatomic. At liquid air temperature the helium and neon in the air remain very largely unabsorbed by charcoal. Sir W. Ramsay* has determined in this way the proportion of these gases in the atmosphere and found 17 parts per million of the two gases together. An earlier determination made by Dewar,† without the use of charcoal, was identical with this. The figures obtained by Ramsay, however, are for the total gases left uncondensed by charcoal at liquid air temperature, and have a direct bearing on the present question. Now, as Lord Blythswood and Allen‡ have shown, there is no difficulty in exhausting an X-ray bulb by the use of cooled charcoal from atmospheric pressure to the point at which it is difficult to force a discharge through the bulb. Yet the pressure of the helium and neon in the bulb must be 17 millionths of the initial pressure or about 1/75 of a millimetre. This result, although appearing strange by itself, is consistent with the experiment on the pressure of argon necessary to allow the discharge to pass. When any method of measuring the amount of gas remaining in the exhausted space other than the electrical is employed, the deficiencies of the non-conducting vacuum produced by cooled charcoal, when the vessel was originally filled with air at atmospheric pressure, become at once apparent. If, for example, the degree of vacuum obtained is measured by the rate of evaporation of liquid air in a Dewar flask, then the presence of these residual monatomic gases becomes all important. Experiments of a quantitative character on this subject are being made by Mr. Berry§ in this laboratory.

[*Added.*—Lord Blythswood and H. S. Allen,‖ after showing, in the first part of their paper, that an X-ray bulb could be exhausted by cooled charcoal from atmospheric pressure in one hour to "a vacuum so good that the tube had to be heated in order to allow the discharge to pass through it," describe in the second part experiments in which the final pressures realised were measured by means of a McLeod gauge. When the apparatus was exhausted by a Fleuss pump initially to 40 mm., the final pressure attained was 0·0009 mm., whereas, starting from a pressure nearly atmospheric, the final pressure attained was ten times as great. They point out the importance of the preliminary exhaustion when an extremely high vacuum is required, owing to the presence of the less easily condensible gases, hydrogen, helium, and neon, in the air, but do not refer to the

* 'Roy. Soc. Proc.,' A, 1905, vol. 76, p. 111.

† 'Roy. Inst. Proc.,' 1902, vol. 17, pp. 223—230.

‡ 'Phil. Mag.,' October, 1905, p. 497.

§ See addendum to this paper.

‖ *Loc. cit.*

apparent inconsistency between the results with the McLeod gauge and their earlier ones with the electric discharge test.

I was present at the meeting of the Philosophical Society of Glasgow (March 22, 1906), when Mr. Allen showed experimentally the exhaustion of an X-ray bulb from atmospheric pressure by cooled charcoal, and I was much impressed at the time with the apparent inconsistency between this result and the recent measurements of Sir W. Ramsay already cited.

The allusions in this section to the results of use of the charcoal method have reference solely to the phenomenon of the bad conducting quality of the residual inert gases that remain when air is absorbed from atmospheric pressure by use of charcoal or other methods. The question of the degree of vacuum produced under proper conditions for obtaining the best results is, of course, entirely different. Although the test of non-conductance, which has, so far, been relied upon too implicitly for gauging the goodness of the vacuum,* is useless, and may be actively misleading in the case of vacua obtained by the use of cooled charcoal without preliminary exhaustion by a pump, there is no doubt at all that, with suitable procedure, this method can give a very high degree of exhaustion.†]

XI.—*Quantity of Pure Helium Detectable by the Spectroscope.*

Mixtures of known composition were made of helium and oxygen, and known quantities introduced into the calcium absorbing apparatus of known volume. The pressure of the residual helium could thus be calculated. In one case 0·13 c.c. of helium was made up to 104 c.c. with oxygen, so that the mixture contained 1/8 per cent. of helium. Successive quantities, each of 0·13 c.c., were introduced into the apparatus, the volume of which was 89 c.c., including an ordinary Plücker tube of volume 4·5 c.c. The following observations are extracted from the note-book. The "quantities" referred to are each 0·13 c.c. of the mixture, and the test of non-conductance was an alternative spark-gap of 2·5 cm. in air.

1st quantity.—Glimpse of D_3 for a fraction of a second as the oxygen spectrum suddenly cleared and tube became non-conducting.

2nd quantity.—D_3 clear while the tube conducted, which was but momentarily.

3rd quantity.—D_3 very pure and distinct, but tube became non-conducting.

5th quantity.—D_3 at first brighter than the mercury yellows.

6th quantity.—D_3 the brightest line at first except for the oxygen orange-red line.

* Compare also G. Claude and René J. Lévy, 'Comptes Rendus,' 1906, vol. 142, p. 876.

† *Cf.* the experiments described by Mr. Berry in the addendum to this paper.

7th quantity.—Just before the non-conducting point the general spectrum was plainly recognisable as helium.

8th quantity.—The brighter helium red (6677) visible.

9th quantity.—The two blues and violet seen.

10th quantity.—First glimpse of the peacock-green line (5016).

Tube took four minutes before it became non-conducting.

11th quantity.—Eight minutes before non-conductance.

13th quantity.—The helium spectrum was now quite good while it lasted, but the tube became non-conducting in three minutes.

The experiment was continued without much alteration up to the point at which 35 quantities had been added. The helium spectrum was plain, and indeed brilliant, so long as the tube conducted, but always a point was reached at which the discharge refused to pass. Diffusion was hastened by alternately heating and cooling the furnace. At the 35th quantity the tube conducted one way of the commutator and not the other, and this was taken as the limiting value. Later in the day and next morning the tube showed the same result. The discharge just passed, but the spectrum was feeble. The line D_3 was clear and the peacock-green exceedingly faint. These were the only helium lines visible.

The pressure of helium corresponding to each dose is 0·0014 mm. and to 35 doses 0·049 mm. It is thus clear that pure helium at a pressure of less than 1/20 mm. is non-conducting to the discharge, while far less than this can be detected in presence of other gases. Like mercury vapour and krypton, a very small trace is visible in the spectrum of another gas. In the above experiments the D_3 line was visible plainly when only a single dose was added, so that to get the minimum quantity detectable a fresh series of experiments with more dilute mixtures was necessary.

XII.—*Most Favourable Conditions for the Detection of Infinitesimal Quantities of Helium.*

Collie* states that in presence of large quantities of mercury vapour the blue helium line, 4922, is the most delicate test for helium, and can easily be seen when none of the other helium lines are visible. It is likely, however, that the author mistook for helium a line in the spectrum of mercury which has the wave-length 4916·4 (Stark) and which is prominent in the mercury vapour-lamp spectrum. It is not often seen in the Plücker tube, except when the latter is warm and liquid mercury is present, so that the vapour pressure of the mercury is considerable. Collie has suggested

* 'Roy. Soc. Proc.,' 1901, vol. 71, p. 25.

for the calibration of spectroscopes a tube containing liquid mercury, helium, and hydrogen, as the spectrum consists of a large number of standard lines fairly equally distributed throughout the length of the spectrum. In such a tube I kept the blue line in question under close observation in a good spectroscope. With a feeble discharge, the tube cold and the mercury spectrum faint, this line was single and due to helium only. As the strength of the discharge was increased, and the tube warmed, the mercury spectrum intensified, and a second line became visible on the more refrangible side of the helium line and distant from it roughly about as far as D_3 is distant from D_2. On still further increasing the strength of discharge the helium line disappeared entirely, and the line was again single and due to mercury only. On diminishing the discharge and allowing the mercury vapour to recondense, the less refrangible line reappeared and grew in strength as the other faded, and finally alone remained visible. Thus, it is clear that so far from enhancing the strength of the helium line, 4922, the presence of mercury serves to mask it completely even in presence of considerable quantities of helium. This line, 4916, is seen equally well in a tube containing mercury in which no helium has been introduced. Under no conditions tried has the line 4922 been seen when D_3 was invisible. The latter is by far the most delicate test for the presence of helium, and becomes visible with a quantity many times less than suffices to develop any other line in the spectrum.

Some experiments with various kinds and sizes of spectrum-tube, some with aluminium and others with platinum electrodes, showed that with minimal quantities of helium at similar *pressure* it is slightly easier to detect the D_3 line in the ordinary Plücker tube of volume 4·5 c.c. than in a tube of minimum volume. But the difference is not great, and is mainly due to the sodium lines from the glass being more prominent in a tiny tube masking the D_3 line. Certainly, when the object is to detect the smallest possible *quantity* of helium, the tube should be of as small volume as possible. A series of experiments was tried in which quantities of helium, far smaller than those necessary to allow the discharge to pass when in the pure state, were examined in presence of hydrogen and oxygen. A mixture containing 0·015 per cent. of helium with oxygen was prepared by the principle of successive dilutions. Known quantities were introduced into the calcium absorption apparatus of known volume. After the oxygen had been completely absorbed, connection between the spectrum-tube and the absorption chamber was closed, and traces of oxygen and hydrogen introduced into the gas in the spectrum-tube. This was accomplished by heating a trace of solid potash, previously fused and freed from water,

in vacuo, or by momentarily raising to redness a spiral of platinum wire by means of a current. It does not appear to make much difference which gas is added to conduct the discharge. After the first momentary heating platinum gives oxygen free from hydrogen. The potash gives hydrogen, doubtless as water vapour. The function of this gas is merely to cause the discharge to pass. Once established, a large part, perhaps the larger part, of the current is carried by the helium, the spectrum of which, under these conditions, appears with extraordinarily minute quantities.

With an ordinary Plücker tube and an apparatus of volume 111 c.c. after three doses, each of 0·13 c.c. of the 0·015-per-cent. mixture, D_3 was but momentarily visible, and could not be again brought out by introducing oxygen or hydrogen. With four doses D_3 was faint but clear and permanent, and this may be taken as the extreme limit of visibility. The partial pressure, due to the helium at this stage, is only 1/100 of that necessary to conduct the discharge when pure, being 0·0005 mm. as compared with 0·05 mm. for the case of the pure gas discussed in the last section.*

If a vacuum-tube of 0·3 c.c. volume is used, it follows that a quantity of helium, 1/4000000 part of a cubic centimetre, measured at normal temperature and pressure, would be within the range of detection by the spectroscope. For safety a margin of twice this quantity should be allowed, or 1/2000 of a cubic millimetre. This quantity weighs 10^{-10} gramme, and contains about 2×10^{13} atoms. The delicacy of the test may be indicated by the following consideration. It can be calculated on the assumption that the α-particle is an atom of helium, that a kilogramme of uranium nitrate would generate 1 c.c. of helium in a period of about 5000 years. The amount of helium produced in a single day should be within the range of spectroscopic detection. Researches on the production of helium from uranium and thorium have been in progress for some time, and it is hoped, now that the ground is cleared, that the matter will soon be put to a definite quantitative test.

In the above experiments the actual quantity of helium used was, of course, many times the amount finally examined in the spectrum-tube. It is easy, however, to fill the absorption chamber after cooling completely with mercury, and to compress the gas into the spectrum-tube. In this

* [The point was raised in the discussion of the paper, how far it had been actually proved that the inert gases were not absorbed, at least in part, by the walls and electrodes. The last experiment answers this question, for in a tube containing only one-hundredth of the quantity of helium necessary to conduct the discharge in the pure state, the helium spectrum may be brought out afresh by introducing a minute quantity of hydrogen or oxygen, which would not have been the case if the helium had been absorbed when the tube became non-conducting.]

operation the minute quantity of hydrogen left unabsorbed by the calcium is, after the compression, just of the right amount to conduct the discharge and to reveal any trace of helium without any additional arrangement.

As an example of an actual experiment, one may be taken from the note-book from an examination of the gases present in native platinum. On the view that the scarcity of an element, after prolonged and extensive search for it, justifies the suspicion that it may be a member of a disintegration series, it was thought possible that evidence of such disintegration might appear in the presence of rare gases in platinum, as is the case with the radio-active minerals. Messrs. Johnson and Matthey very kindly lent me as much native platinum as required, and I desire to acknowledge my indebtedness to them for their kindness.

In one experiment a quantity of about 300 grammes was heated in a porcelain tube in an electric oven to 1200° C., and the gases passed into a calcium absorption chamber of the usual kind provided with a tiny spectrum-tube at the upper end. A trace of carbon dioxide, from the walls probably, first came off. Then nitrogen appeared, and, as the temperature approached 800° C., carbon dioxide in quantity. On closing the connection with the platinum and absorbing the gas with calcium, the spectrum-tube became quite non-conducting. These operations were repeated, the gas evolved being admitted and absorbed in stages. When the electric oven had reached a temperature of 1000° C., a momentary glimpse of the D_3 line was seen. At 1100° C. the peacock-green line was picked up, and the more prominent of the two reds seen extremely faintly. On forcing the discharge the argon greens could be faintly made out in a Ramsay pocket spectroscope. When the oven reached 1200° C., a large quantity of carbon dioxide had accumulated. This was admitted to the absorption chamber, and the connection sealed and the heating of the platinum stopped. On cooling the calcium after absorbing the gases, the spectrum-tube was on the verge of non-conductance, but extremely faint helium could be detected. Mercury was admitted and the contents compressed completely into the tiny spectrum-tube. The helium spectrum was now reasonably bright, all the lines being visible, together with the hydrogen red and the mercury lines. With the pocket spectroscope argon could just be detected. It was estimated from the appearance of the discharge at various stages of the compression that about 1/5 of a cubic millimetre of helium was present, a quantity 400 times as much as could have been detected, yet only representing 1/15000000 per cent. by weight of the platinum. The experiment lasted but two hours, and is given merely as an example of the ease with which an infinitesimal quantity of helium may be separated from large amounts of other gases

by means of calcium, and its quantity estimated with fair probability. No weight is to be put on the result as indicating the origin of the helium. As a matter of fact, the native platinum was quite distinctly though feebly radio-active, 300 grammes of it in an electroscope producing an effect equivalent to 0·07 milligramme of uranium oxide. Clevite usually contains about 2 c.c. of helium per gramme, and is usually of about the same activity as uranium oxide. The platinum contained about 3,000,000 times less helium, and was about 4,000,000 times less radio-active than clevite, so that there is no reason to go further to explain the source of the helium than to suppose that a trace of some radio-element is present in native platinum.

Appendix.—*Results of Gauging High Vacua by the Evaporation Test.*

By Arthur John Berry.

In this note the results of some experiments, on the rate of evaporation of liquid air contained in a Dewar vessel exhausted in different ways, are described with the view to showing that this test may be used as a means of gauging the degree of vacuum produced by different processes. Owing to various causes the research has not been carried as far as it was intended, but one set of measurements, complete in themselves, have been obtained, which bear out in a clear manner one of the points discussed by Mr. Soddy in the paper preceding. Starting with a vessel filled with air at atmospheric pressure, there is no difficulty, by using the method of Sir James Dewar to produce a vacuum therein, in obtaining a vacuum apparently perfect, so far as the electric discharge test can indicate, provided that a sufficiency of charcoal is employed. It was of interest to compare the rate of evaporation of liquid air in a Dewar vessel exhausted in this manner with the rate in the same vessel exhausted also by Dewar's method, but in which the air had been first removed by an auxiliary pump. Although the electrical test reveals no difference in the degree of vacuum obtained in the two methods, it is to be expected that the thermal test will show a far higher vacuum by the second method than by the first, owing to the residuum of non-conducting inert gases left by the first method.* This expectation has been fully borne out by the experiments.

The vessel employed was of about 1 litre capacity, globular in form, and silvered on the two inner walls. During the exhaustions it was placed in an inverted position in an air oven, and the temperature maintained at

* Compare Lord Blythswood and H. S. Allen, 'Phil. Mag.,' October, 1905, p. 497.

350° C. A vacuum-tube served to indicate the progress of the exhaustion. At the completion of each exhaustion it was filled with liquid air, and kept in an ice chest to keep the external temperature constant. The vessel was weighed at regular intervals to determine the rate of evaporation of the air. Three different methods of exhaustion, designated throughout I, II, III, were employed.

I. In the first the exhaustion was performed by the mercury pump. A Töpler pump of ordinary pattern, worked by hand, was used, and pumping was continued from four to five hours while the vessel was heated in the air oven. The pump had a capacity of about 450 c.c., and was provided with a phosphorus pentoxide tube and tap. The results of two similar experiments agreed well among themselves, and in the table the second of the two, which was slightly the better, is alone included.

II. In the second method the apparatus was exhausted from atmospheric pressure by cooled charcoal. As in the experiments of Lord Blythswood and H. S. Allen,* two separate charcoal bulbs were employed, the one with 97 grammes and the other with 70 grammes of charcoal freshly prepared from cocoanut shells. The first bulb alone reduced the pressure from atmospheric to the fluorescent stage in 30 minutes, and was then cut out and the second bulb brought into action. The absorption was continued one and a-half hours further, and the vessel sealed off. No discharge could be sent through the vacuum-tube at this stage.

III. The same vessel was exhausted by a duplex Fleuss pump of large size, mechanically driven, and during the action of the pump the charcoal was well heated. In this way carbon dioxide is expelled from the charcoal, and the last traces of air are swept out. It was found in a separate experiment that little or no difference was produced in the result by the displacement of the last of the air by oxygen during pumping. In this method only one charcoal bulb was used, which was connected direct by a glass tube without taps to the vessel being exhausted. The connection with the pump was sealed after the removal of the air was judged complete, and the absorption by charcoal continued for two and a-half hours.

The following table shows the results of the three methods. Weighings were taken at intervals of either 6 or 12 hours. The first column shows the time in hours from the first weighing, and the total weight of liquid air initially present in the three experiments is indicated in the first line. The succeeding lines indicate the amount that has evaporated in the 6- or 12-hour interval from the previous weighing :—

* *Loc. cit.*

Hours.	I.*	II.	III.
0	972 grammes	954 grammes	979 grammes
12	2 × 54·5	2 × 63	2 × 40·5
18	54	63	40
24	54	60	39
36	2 × 54·5	2 × 60	2 × 39
42	54	59	39
48	55	58	37
60	2 × 56	2 × 57·5	2 × 37
66	56	57	37
72	57	56	37
84	2 × 58·5	2 × 56	2 × 37
90	58	55	38
96	59 (78 remaining)	56 (18 remaining)	36
108	—	—	2 × 37
114	—	—	38
120	—	—	36
132	—	—	2 × 36
138	—	—	36
144	—	—	37 (78 remaining)

It will be seen at a glance that whereas the vacuum resulting in the second method, by cooled charcoal, but starting from atmospheric pressure, is inferior to that produced by a simple mercury pump, that obtained in the third method, by charcoal after removal of the air, is by far the best of the three. After six days 78 grammes of liquid air out of the original kilogramme remain in the vessel.

In conclusion, I desire to take this opportunity of expressing my indebtedness to Mr. Soddy, at whose suggestion the research was undertaken, for placing the apparatus required at my disposal and for many valuable suggestions.

* The slight increase in the rate of evaporation during this experiment is due to a shortage in the supply of ice in the ice-chest. In the other two experiments the chest was kept well filled.

The Theory of the Compositions of Numbers.—Part II.

By Major P. A. MacMahon, F.R.S., etc.

(Received August 23,—Read December 6, 1906.)

(Abstract.)

This investigation was recently suggested to the author by Professor Simon Newcomb.

A pack of cards is shuffled and then dealt out in succession, the cards being placed in one heap or pack so long as the numbers of pips on them are in ascending order (equality in the numbers of pips counting as ascending order); when there is a break in ascending order, a fresh heap or pack is commenced, and so on.

In this way a set of s packs will be formed containing

$$a_1, a_2, \ldots, a_s$$

cards respectively.

If the total number of cards be n, it is clear that the succession of numbers

$$a_1, a_2, a_3, \ldots, a_s$$

constitutes a "composition" of the number n into s parts.

Denote by $\mathrm{N}(a_1 a_2 \ldots a_s)$

the number of arrangements of the cards which yields the composition

$$(a_1 a_2 \ldots a_s),$$

and by N_s

the number of arrangements which yields compositions into s parts.

The investigation is primarily concerned with the properties of the numbers

$$\mathrm{N}(a_1 a_2 \ldots a_s),\ \mathrm{N}_s$$

(1) When no two cards in the complete pack have the same number of pips;

(2) When the cards are numbered in any manner whatever.

This investigation is essentially a contribution to the Theory of the Compositions of Numbers.

The method employed is "the powerful calculus of symmetric functions." The associated differential operators are freely used, and a complete solution of the main problems of the paper is presented.

Incidentally some useful and novel ideas in the pure theory of symmetric functions are reached and developed.

In regard to the roots of the equation

$$x^n - p_1 x^{n-1} + p_2 x^{n-2} - \ldots = 0,$$

a new symmetric function

$$p_{rs}$$

is defined by impressing a multiplication theorem upon the elementary functions

$$p_r, p_s;$$

viz., I write

$$p_r p_s = p_{rs} + p_{r+s},$$

and generally

$$p_{r_1 r_2 \ldots r_\beta} p_{s_1 s_2 \ldots s_m} = p_{r_1 r_2 \ldots r_\beta s_1 s_2 \ldots s_m} + p_{r_1 r_2 \ldots, r+s_1, s_2 \ldots s_m};$$

and in regard to the homogeneous product-sums

$$h_r, h_s$$

similarly,

$$h_r h_s = h_{rs} + h_{r+s}$$

$$h_{r_1 r_2 \ldots r_\beta} h_{s_1 s_2 \ldots s_m} = h_{r_1 r_2 \ldots r_\beta s_1 s_2 \ldots s_m} + h_{r_1 r_2 \ldots r_\beta + s_1, s_2 \ldots s_m}.$$

The main question concerning the numbers

$$\mathrm{N}(a_1 a_2 a_3 \ldots a_s)$$

is solved by means of the symmetric function

$$h_{(a_1 a_2 \ldots a_s)};$$

and I obtain the important theorem

$$h_{(a_1 a_2 \ldots a_s)} = p_{(a_1 a_2 \ldots a_s)'},$$

where

$$(a_1 a_2 \ldots a_s), \quad (a_1 a_2 \ldots a_s)'$$

are conjugate compositions of n.

The composite conjugate to a given one is readily obtained from the nodal graph of a composition given for the first time in this paper.

As an illustration, the graph of the composition

(271)

is given by

. .
. . . . . .
.

each row of nodes commencing vertically beneath the right-hand node of the previous row. The conjugate is thence obtained by reading the columns from left to right, viz.:—

(12111112).

The Theory of Photographic Processes, Part III: The Latent Image and its Destruction. (Abridged Account.)

By S. E. SHEPPARD, D.Sc., and C. E. K. MEES, D.Sc.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received September 19,—Read December 6, 1906.)

The following abridged account summarises the results of an investigation to be published in a more extended form subsequently. It deals with the formation of so-called "latent images" on photo-films, their destruction by chemical agents, and the bearing of these results upon the nature of the ight-product in silver halides and its function in promoting reduction.

PART I.—*The Developable Condition in Halide Emulsions.*

The essential chemical reaction in development may be typified by the equation $Ag + R'' \rightleftarrows Ag\,(met.) + R'$. It is somewhat difficult to give a comprehensive and characteristic definition of development which shall distinguish it from normal reduction of silver ions to the metallic state, the more so that the word develop is used in such varied senses. For present purposes the following is probably sufficient. Developability is brought about when a preliminary treatment accelerates a subsequent reduction with reducing agents. It is, perhaps, impossible to draw a line of strict demarcation, but the inner mechanism will be clearer in the sequel. An investigation by one of the authors* has shown that the aforementioned reaction in development is reversible. Independently, then, of "developability" the reaction $Ag + R'' \rightleftarrows Ag + R'$ proceeds to a state of equilibrium. But it does not follow that metallic silver is precipitated. Unless the potential of the reducing ion is very high, the metallic silver may remain in solution. Two further eventualities are possible. A *colloidal* silver solution may be formed, stable under certain conditions, but liable to coagulation by electrolytes. Or there may be some cause lowering the meta-stable limit, so that metallic silver is precipitated. In the presence of solid silver with normal reducing agents complete reduction of the gelatino-halide grain is ensured,† in agreement with the "silver-germ" theory of development.‡ *Any cause tending to lower the meta-stable limit of the silver solution makes the halide developable.* The aforementioned investigation showed that the reduction in

* 'Chem. Soc. Trans.,' 1905, vol. 87, p. 1317.

† 'Roy. Soc. Proc.,' A, 1905, vol. 76, p. 217: "Theory of Photographic Processes, Part II.

‡ 'Chem. Soc. Trans.,' *loc. cit.*

development could be divided into two periods, an initial induction, the length of which depended chiefly on chemical processes, and a second period, in which the velocity depends chiefly on the supply of reducing ions to the affected grains.

A number of substances, if introduced into the grain in very intimate mixture—probably as a solid solution*—can greatly shorten the induction period and bring about developability. We found that the following could act as "germs" for a dry-plate:—

(*a*) *Silver*, introduced as colloidal silver by treatment with silver nitrate solution and then Carey Lea's ferrous citrate solution. Dilute HCl was then applied, converting the colloidal silver to metallic, and in a developer reduction proceeded forthwith.

(*b*) *Gold*, by the action of gold chloride on the gelatin film.

(*c*) *Platinum*, to some extent as with gold, and better by the action of ferrous oxalate.

(*d*) *Silver sulphide*, by the action of polysulphides and of acid thiosulphate with ferrous oxalate.

(*e*) *Gas ions* from flame gases with a plate soaked in developer.

That the shortening of a chemical induction period by lowering the meta-stable limit is the essential factor in developability appears to be confirmed by the following. Gelatino-silver nitrate, jellified with 10-per-cent. gelatin, gave, with certain precautions, on treatment with ammoniacal pyrogallol, or better, ferrous fluoride, rings of metallic silver deposited at regular intervals, in addition to a general coloured deposit. The former are the well-known Liesegang's rings,† considered by Ostwald as a confirmation of his theory of a meta-stable limit, and quantitatively investigated for silver chromate by Morse and Pierce.‡

Non-emulsified Silver Halide and the Function of Gelatin.—An investigation of the action of light and reducing agents on pure precipitated silver bromide layers confirmed the statements of Abney and Schaum,§ that gelatin mechanically or chemically retards reduction by developers. Now, Jaffé,‖ in some studies on supersaturation, found that the "life" of a solution was always prolonged by repeated preliminary filtration. The removal of "germs" mechanically raised the meta-stable limit. Our experiments point to the gelatin functioning as a protective sheath against "germ infection," thus

* *Cf.* H. Weisz, 'Zeit. phys. Chem.,' 1906, vol. 54, p. 305.

† 'Chemische Reaktionen in Gallerten' (Düsseldorf).

‡ 'Zeit. phys. Chem.,' 1904, vol. 45, p. 600.

§ 'Zeit. wiss. Phot.,' 1904, vol. 1, p. 377.

‖ 'Zeit. phys. Chem.,' 1903, vol. 43, p. 565.

mechanically retarding reduction. In part, also, it forms solid solutions with the halide, and complex ions with the silver ion, both additional helps to the stability of the halide.

On the whole, the evidence tends to the conclusion that a necessary and sufficient condition for "developability" is the production in the silver halide grain of a *new* substance. Now, the developable condition may be induced by the action of various energies, which we may group as follows* :—

(*a*) Ether vibrations, from infra-red to ultra-violet.
(*b*) Röntgen rays, kathode rays, and the β- and γ-radiation of radio-active bodies.
(*c*) Mechanical stress or pressure.
(*d*) Heat.
(*e*) Chemical action.

At present we will only consider the first, resulting in the ordinary photographic image. To deal critically with the various theories, physical and chemical, as to its nature, would take too much space. But it is almost impossible to account for the way in which the "latent" image interferes with certain definite chemical reactions on any physical theory. Such are the aforementioned abbreviation of an induction in reduction, the existence of an image capable of development after fixation, and, in particular, the destruction of the "latent" image by halogenising and oxidising agents. We have made a somewhat extended investigation of the action of the latter and may collect our conclusions as follows.

Part II.—*The Destruction of the "Latent" Image.*

Section A. *The Action of Oxidisers Subsequent to Exposure.*

It has frequently been maintained that halogenising and oxidising agents do not actually destroy the latent image, but only retard development. Sterry,† for example, considered that their effect was to delay what he termed "secondary development," *i.e.*, an assumed intensification of a primarily formed image by silver from neighbouring granules. Our experiments with chromic acid subsequent to exposure led to the following conclusions:—

Plates were dipped by rotation in CrO_3 solution for a given time, then rinsed by rotation, and developed.‡ The plate-curve was distorted at the top, but

* See also C. Lea, 'Phil. Mag.,' 1891, p. 320.

† J. Sterry, 'Phot. Journ.,' 1904, vol. 54, p. 50.

‡ For the authors' experimental methods, and for the meaning of the symbols $\log i$ and γ_∞, etc., see the previous papers, 'Roy. Soc. Proc.,' 1904, vol. 74, p. 447, and A, 1905, vol. 76, p. 217.

log i and γ_∞ were unchanged. The velocity-constant K of development was diminished, approximately in proportion to the *logarithm* of the strength of the preliminary CrO_3 bath. Prolonged washing never entirely annulled the effect, but it was diminished. The values of K (the velocity of development) decreased with the time of immersion in CrO_3, ultimately reaching a minimum for each concentration, the function of the effect on K being independent of the concentration.

From these facts we conclude that the CrO_3 is irreversibly absorbed in the film, probably both to the film and to the silver halide, forming with the latter something of the nature of a solid solution. Freshly precipitated AgBr is coloured yellow by chromic acid, and the colour is not removed by long washing. The retained oxidiser then slows development by oxidising the developer in the film. This view was further confirmed as follows. Plates were treated, after "chromating," with a solution of sodium sulphide, which restored K to its normal value by reducing the chromic acid.

This "sulphite reaction" enabled us to decide without doubt that the prolonged action of CrO_3 destroyed the latent image, *i.e.*, both log i and γ_∞ were altered. *After* sulphiting, since K is now restored to its normal value, any change in γ is due to a lessening of the mass of the latent image. The following table exemplifies the results for N/50 CrO_3, with a subsequent bath of N/10 Na_2SO_3, all developed in M/20 quinol for five minutes:—

t = time of immersion in CrO_3 in minutes.

	$t = 0$.	2.	20.	40.	120.
γ	1·65	1·65	0·77	0·48	0·34
log i.....	1·25	1·25	1·30	1·50	1·80

The rate of attack on the latent image was found to increase very rapidly with the concentration of the CrO_3. The phenomena point to a re-oxidation (possibly involving the release of halogen from a combination with gelatin) of a reduction product, the latter being in solid solution in the normal halide.

Section B. *Desensitisers.*

Plates bathed before exposure in certain metallic salt solutions show a diminished sensitiveness to light, even after prolonged washing.* We find that salts of the following cations are effective, the anion being unimportant:—$Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $(UO_2)^{\cdot\cdot}$, whilst the following have no action:—$H^{\cdot}$, $K^{\cdot}$, $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Mo^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$ (?), $Ag^{\cdot}$, $Pb^{\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$. If plates are dipped in $CuSO_4$ immediately prior to development with FeC_2O_4, there is no action. If left standing, γ_∞ is lowered, the latent image being destroyed in a

* Lüppo-Kramer, 'Wiss. Arb. auf d. Geb. d. Phot.' (Knapp, Halle).

manner similar to the action of chromic acid. But if dipped before exposure, the value of log i is greatly increased, *i.e.*, the sensitiveness diminished, but γ_∞ and K remain unchanged.

The peculiar behaviour of desensitisers might be referred to two categories: either (*a*) it alters the sensitive salt prior to exposure; or (*b*) it occurs during exposure by reversal of the photo-chemical reaction. The first would agree with that theory of "ripening" which supposes this process produces a minute quantity of the photo-reduction product. The second requires that some of the desensitising salt be retained in spite of prolonged washing, a view confirmed by some experiments with metol development. The following experimental results, with ferrous oxalate development, fully bear out the theory that *desensitisers act during exposure by reversal of the photo-chemical action*, and not by any modification of the sensitive substance:—

(i) *Moist and Dry Films.*—We have confirmed Sterry's result: that moist films are less sensitive than dry ones, but have a higher γ_∞.

(ii) *Time of Immersion and Concentration.*—The effect, as measured by $\Delta \log i$, increases with the time of immersion, and on prolonged immersion weak solutions give the same effect as strong ones. Conversely, different solutions, acting for the same time but with long washing out, give the same effect. Otherwise this depends on the concentration and time.

(iii) *Re-sensitising.*—By the action of a solution which combines with or reduces the desensitising ion, partial or complete resensitising may be obtained. With copper salts, quinine and benzaldehyde act in this manner; with ferric ions, oxalate solution, the ferric complex not being so effective.

Hence it appears probable that the desensitiser forms a solid solution or some combination with the silver salt, the maximum effect being for the limiting quantity absorbed. For the relative effect the following results were obtained:—

Plates bathed in.....	Water.	$CuSO_4$.	$(UO_2)(NO_3)_2$.	$FeCl_3$.	$HgCl_2$.
Log i	$\bar{1}$·95	0·50	0·59	1·79	not > 2

Hence extent to which plate is made insensitive—

—	3·6	4·4	69	> 100

The Mechanism of Desensitising.—It is noteworthy that an effect may be obtained with very slight concentrations. Thus with M/100,000 $CuSO_4$, with two hours' immersion before exposure, we obtained log i (unbathed) 1·60, log i (bathed) 2·25.

Hence, the desensitising effect of water is probably to be attributed to small quantities of impurities, and the action may give the clue to some of the troubles met with in emulsion-making, where the sensitiveness is sometimes found to drop for unknown reasons.

Further, if a plate containing $CuSO_4$ be exposed long enough to overcome the resistance introduced by the $CuSO_4$ and so give a full density, after a time the image again disappears. A very small quantity of the desensitiser can thus continually destroy the latent image. The action may be described as catalytic. The metallic ions effective are all known to act as catalysts in oxidising and halogenising processes.* Substances such as stannous salts, quinine, mannite, etc.,† inhibit the positive catalysis by reacting with the catalytic ion, and hence acting as negative catalysts. The catalysis is to be referred probably to pseudo-catalysis or "Uebertragungscatalyse" (Wagner, Ostwald), since the copper probably takes a definite part in the reaction according to some scheme of the form—

$$a \ldots\ldots\ldots \quad Cu^{\cdot\cdot} + Ag \text{ (resp. } Ag_2^{\cdot}) = Ag^{\cdot} + Cu^{\cdot},$$
$$b \ldots\ldots\ldots \quad Cu^{\cdot} + \tfrac{1}{2}O_2 = Cu^{\cdot\cdot} + O'',$$

the reformed $Cu^{\cdot\cdot}$ again taking part in the destruction of the image.

During exposure, this reversing action prevents the formation of the reduction product. The effect would be different after exposure, owing to the reduction product forming a solid solution in normal halide. This view of a catalysis of a reverse action was confirmed by an increase in the *intermittency failure* in presence of a desensitiser.

Section C. *The Spontaneous Decay of the Latent Image.*

Much evidence has been brought forward pointing to a spontaneous decay of the latent image,‡ with which we may associate the phenomena of "reversal," and the failure of the Bunsen-Roscoe reciprocity relation, which states that the photo-chemical effect of an exposure E is the same whether the intensity or the time be altered, provided $It = E$ be constant.

Abney§ and others have shown that this law does not hold absolutely for photographic plates, but that there is a range giving the maximum available energy. Repeating the work in a different manner, we used a very wide range of intensities. A typical table is as follows:—

* Bredig, 'Zeit. phys. Chem.,' 1903, vol. 46, p. 502; Titoff, *ibid.*, 1903, vol. 45, p. 641.

† Bigelow, 'Zeit. phys. Chem.,' 1898, vol. 27, p. 585; and Titoff, *loc. cit.*

‡ *Cf.* Backeland, 'Zeit. wiss. Phot.,' 1905, vol. 3, p. 58.

§ 'Phot. Journ.,' 1893.

I.	t (to give D = 1) in secs.	It.	log (I × 1000).
84·5	0·204	17·2	4·927
6·0	2·59	15·5	3·720
1·71	9·61	16·4	3·232
0·452	34·4	15·5	2·655
0·130	120	15·5	2·114
0·198	931	18·4	1·296
0·0074	4760	35·1	0·869
0·0056	6400	36·2	0·750

The deviations are best shown as follows: if the values of It, which gave an equal effect (density) be plotted against those of I, or, for convenience, log I, then the resultant curve will, if there be no deviation, be a straight line parallel to the x axis, but otherwise a curve showing the nature of the deviations. (Compare Amagat's pv-p curves.) It was found that:—

(a) The failure is not a steady function of t.
(b) Is independent of the total value of It.
(c) Is relatively independent of the sensitiveness of the plate, *i.e.*, starts at the same point relatively to the inertia point.*

The Intermittency Failure.—Another form of reciprocity failure is with intermittent exposure, and this has been investigated by Abney and Englisch.† Our results are in good qualitative agreement with these observers', whilst practically they show that in sensitometry sector-wheels should not be driven at more than 100 revolutions per minute, the error below this being negligeable. The general conclusions are:—

(i) The failure increases with the pause between each illumination, increasing as the sector-angles diminish.
(ii) It increases with the *rate* of intermittency.
(iii) It is greater with small intensities.

Englisch attributes the failure to an initial induction and also to a "fading-loss" or deduction. This latter merits chief consideration. Various "molecular" and "strain" hypotheses have been suggested, but the peculiar nature of photo-chemical equilibria appears to give sufficient explanation. Abegg‡ has correlated these phenomena with the lessened photo-effect obtained when plates are exposed through the glass side. From the

* This is opposed to Abney's results, and possibly requires further confirmation; our results are for plates of 20 and 200 H. and D. Experiments with "gas-light" emulsion are desirable, but difficult, owing to the great exposures required.

† 'Schwarzungs-Gesetz phot. Platten.' W. Knapp, Halle.

'Sitz.-Ber. Wien Akad.,' 1900, vol. 109, p. 1.

investigations of Luther* it appears that the continuous exposure of silver halides to light results in a state of equilibrium in which every light-intensity is balanced by a definite halogen potential (whether expressed as gas pressure, solution pressure, or electric potential). Equilibrium is not usually reached in ordinary exposures because these are too short, whilst the halogen is removed by diffusion and combination with the gelatin. Diffusion is easier from the film-air side; to this Abegg attributes the lessened effect through glass.† When the incident light is cut off, the reverse reaction is no longer opposed by the photo-dissociation, and the theory agrees well with the facts brought forward on the intermittency failure. The failure with small intensities is less easily accounted for, and is perhaps involved in processes antecedent to the dissociation of halogen, which will be mentioned later.

Reversal.—The peculiar phenomenon of reversal by very prolonged or intense exposure has not yet received a satisfactory explanation. Experiments with "retarded" development‡ show that the characteristic plate curve does not give a complete epitome of the photo-chemical reaction. In the diffusion period of development§ it is evident that an increase per grain of the photo-reduction product would not accelerate development, whilst if the bromine released were mechanically retained in the film it would oxidise the developer, as was found with chromic acid (see p. 464), hence leading to apparent reversal. The results of Precht‖ with plates containing a developer (edinol sulphite) favour this view, since reversal is then much retarded. Weisz,¶ in a comprehensive study of this phenomenon, has shown that "tanning" theories must be abandoned, and apparently considers that a modification of the physical state of the reduction-germ or nucleus is brought about.

The Nature of the Reduction Product.—So far the evidence only shows, if with some degree of conclusiveness, that the latent image consists of a substance containing less halogen. The "free silver" theory is negatived by the general behaviour of oxidising agents, and especially by that of nitric acid.** By the researches of Luther†† on the halogenisation of silver, the existence of the half-halides Ag_2X is made very probable, as well as their

* 'Zeit. phys. Chem.,' 1899, vol. 30, p. 628.
† *Loc. cit.*
‡ 'Chem. Soc. Trans.,' 1905, vol. 87, p. 1317.
§ *Ibid.*, p. 1316.
‖ 'Zeit. wiss. Phot.,' 1905, vol. 3, p. 79.
¶ 'Zeit. phys. Chem.'
** 'Zeit. wiss. Phot.,' 1905, vol. 3, p. 329.
†† *Loc. cit.*

identity with the visible and latent images, but later investigations by Günter and Baur* show that the half-halide must form solid solutions in all proportions with normal halide. The varying behaviour of different exposures to oxidisers may then be explained as follows: In consequence of the thickness of the film and the absorption of light by this, there exist layers of halide grains with varying amounts per grain of reduction-product. If n grains must be reduced to the metallic state to give a visible image (Schwellenwert), the corresponding exposure will be shifted by reoxidation, progressively with time and concentration, but as the amount of subhalide falls, and its concentration in the grain is lessened, the potential of the oxidiser must be raised, or in the more exposed portions there will still be left sufficient grains with a sufficient minimum of half-halide to ensure developability.

Part III.—"*Ripening*" *and the Photo-electric Effect.*

Before summarising our conclusions on the photographic process we may interpolate a brief note on the process of ripening and on a probable action preliminary to any chemical action in exposure.

Ripening or the raising of sensitiveness by "cooking" aggregates the particles in a well-known manner,† and increases the opacity to light. A possible explanation of the change involved is the following: The vibrations of light are considered to be of an electro-magnetic nature, and their absorption as conditioned by resonance. Previously mentioned researches by Quincke show that in a gelatino-halide emulsion the admixture is of the most intimate kind. Every electro-magnetic resonance is conditioned not only by the electric and magnetic properties of the resonators and *of their surrounding medium*, but also necessarily by their spatial distribution. In fact, the vibration period increases with the spatial extension of the resonators, with the closeness of their packing and with the dielectric constant of the medium.‡ Zsgimondy, by the ultra-microscopic method,§ has shown that gelatin consists of a homogeneous basis containing aggregates or "clumps," the proportion being variable and influenced by the state of the gelatin. In an emulsion these clumps would give their form and distribution to the associated halide. They may be considered as forming the resonators or groups of systems of resonators postulated above, and their formation as one end in ripening. To this is also probably due the slow alteration in the viscosity of gelatin on cooking, noted by Schröder.

* 'Zeit. phys. Chem.,' vol. 45, p. 618.

† *Cf.* Ostwald, 'Zeit. phys. Chem.,' 1900, vol. 34, p. 495.

‡ *Cf.* Luther, 'Zeit. wiss. Phot.,' 1905, vol. 3, p. 264.

§ 'Zeit. Elektrochem.,' 1902, vol. 8, p. 686.

The Photo-electric Effect.—As is well known, certain metals and other substances, under the influence of ultra-violet light, lose a negative charge. The sensitiveness of the effect runs parallel with the absorption and is greatest for the region chiefly absorbed. The silver halides and many dye-stuffs used as sensitisers are highly photo-electric. It is assumed that the incident light sets free electrons or negative corpuscles, which at a bounding surface ionise the gas and are removed by diffusion and convection, or, if in an electric field, move in accordance. There is, however, another photo-electric effect. Many substances, and especially silver and the silver halides, give a difference of potential when immersed in an electrolyte and one pole exposed to light. M. Wilderman,* from a quantitative study of the phenomenon, concludes that the solution pressure of the exposed plate is increased. H. Scholl† finds that silver iodide in light undergoes a species of dissociation which produces the ions of AgI and negative electrons. The latter are much more mobile than the electrolytic ions in solid silver iodide and impart metallic conductivity to this. Hence we must agree that in the photo-film the electron is set free, not only at the bounding surface, but as far through the substance as the intensity of the light is sufficient. This may be regarded as the primary photo-chemical change. Joly‡ has ably resumed the bearing of the photo-electric effect. He considers that the latent image is built up of ionised atoms or molecules and upon these the chemical effects of development are subsequently imposed. But the assumed stability of the free electric charges remains unexplained,§ as also the destruction of the latent image by oxidising agents. Rather does it seem that the liberated electron brings about a chemical change (if temperature and other conditions are favourable) and that the product, when below the threshold of perception, forms the latent image. The process may be typified as follows:—

$$Ag^{\cdot} + Br' + \ominus + G^{\cdot} = Ag\,(met.) + Br + G,$$

or

$$2Ag., \text{ etc.}, \rightarrow Ag_2^{\cdot} \text{ (subhalide theory)},$$

where G is a molecule which becomes positively charged to $G^{\cdot}$ (molion) by the photo-electric process.

Probably many of the phenomena of photographic induction may be susceptible of an explanation by this theory. In addition it accounts for the action of dyes as sensitisers for their own region of absorption, since the electrons liberated from the dye would act as before.

* 'Roy. Soc. Proc.,' 1904, vol. 74, p. 369.

† 'Ann. Phys.,' 1903 [4], vol. 16, pp. 193 and 417.

‡ Address to Photographic Convention, 1905. 'Brit. Journ. of Phot.,' 1905, vol. 52, p. 551.

§ *Cf.* also Scholl, "On the Evanescence of Photo-electric Effect," *loc. cit.*

Summary.

The photographic process, in brief, consists in the passage of ionised silver to the metallic state, with a sub-oxidation stage as probably intermediate. We may summarise our conclusions at the present stage as follows:—

1. *Ripening* due to—

(*a*) Formation of resonating systems.

(*b*) Formation of (intermediate) reduction-product.

Function of gelatin: forms resonators and assists reduction.

2. *Exposure*, light absorbed and electrons set free which ionise the halide and surrounding gas.

Function of gelatin: high dielectric constant, photo-electric, conserves electrons.

Function of gas: according as it removes electrons or not, may diminish sensitiveness. Electrons may be emitted either from halide or from sensitisers.

3. *Ionisation* leads to chemical reduction: electrolytically dissociated halide becomes discharged by interaction with electrons and positive atom or molions.

Function of gelatin: combines with free halogen.

The reduction probably results in a half-halide, Ag_2X, in solid solution. The action is reversible, a definite halogen pressure corresponding to each intensity of light.

Destruction of latent image—

(*a*) Free halogen during and after exposure.

(*b*) Desensitisers during exposure; cyclic action with oxygen involved.

(*c*) Oxidisers after exposure; possibly halogen released from gelatin.

(*d*) Reversal (1) halogen reconverts subhalide; (2) halogen (absorbed) oxidises developer.

4. *Development:* subhalide reduced to metallic silver, silver germ formed and complete reduction consequent on—

(*a*) Formation of silver germs: velocity chiefly dependent on chemical processes; *induction period.*

(*b*) Deposition on silver germ: velocity dependent on diffusion processes *steady state.*

Very possibly subhalide occurs as an intermediate product in development also.

Function of gelatin: filter against germs, so preventing fogging.

5. *Fixation* or removal of remaining halide.*

In conclusion, the authors desire to express their great thanks to Sir William Ramsay, K.C.B., F.R.S., for his constant advice and interest in the investigation.

The Relation between Breaking Stress and Extension in Tensile Tests of Steel.

By A. Mallock, F.R.S.

(Received December 4,—Read December 13, 1906.)

A large number of the tensile tests of steel are now made with test-pieces, which are only a few diameters long (fig. 1).

Fig. 1.

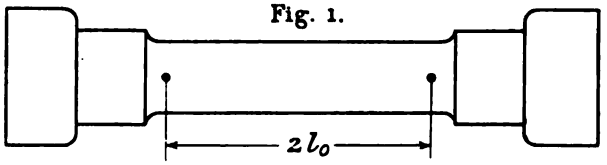
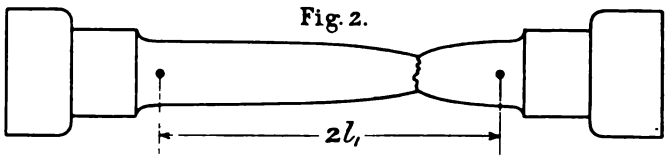


Fig. 2.



When such a test-piece is broken by tension, it has a profile, as shown in fig. 2. The usual records, made when the tests are carried out, include, among other things, "breaking stress" and "extension per cent."

"Breaking stress" here means the maximum tension applied divided by the original area of the test-piece; and extension per cent. is taken as the percentage increase due to the strain, in the distance between two marks, one at either end of the test-piece, whose unstrained distance is known. The use of the term "breaking stress" in the above sense is convenient, from an engineer's point of view, as showing what force a bar, etc., of given sectional area will stand before giving way. The true breaking stress of a material, however, is the actual intensity of the stress at

* 'Phot. Journ.' (Trans. Roy. Phot. Soc.), 1906, vol. 46, p. 235: "On the Theory of Fixation."

the broken surface, and is, of course, greater than the nominal breaking stress, because of the reduced area of the broken surface. To avoid confusion, I will call the true breaking stress the "intrinsic strength" of the material.

An examination of a very large number of observations made with the short test-pieces shows that, if the nominal breaking stress (as defined above) is expressed in tons per square inch, the arithmetical sum, breaking stress + elongation per cent., remains constant, and equal to about 67 or 68 for all mild steels, which, at the beginning of the test, are free from internal mechanical strain, no matter what has been the heat treatment of hardening and annealing to which they have been subjected.

The object of this note is to examine the reason for this: for, since breaking stress has the dimensions of a force ÷ an area, and extension per cent. is a pure number, it seems at first sight that no physical quantity could be represented by their sum.

To determine the relation between breaking stress (B), elongation per cent. (E), and the intrinsic strength of the material, the form assumed by the test-piece when extended must be known.

The experimental fact to be explained is $B + 100E_2 = \text{constant} = 67 \text{ or } 68$, if B is expressed in tons per square inch.

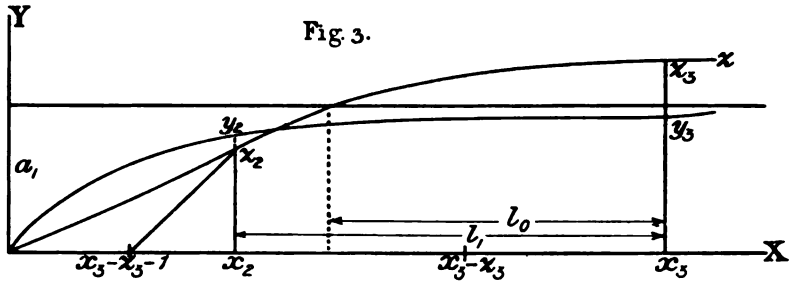
Any relation which makes $dB/dE = -1$ ensures the constancy of the sum of B + E, and a variety of relations might be assumed which will do this approximately; but the particular relation to be sought for is that which not only makes $dB/dE = -1$, but also makes the diameter calculated from E correspond to the measured diameter, not only at the break, but along the whole length of the test-piece.

When the extension is a small percentage of the whole length, the contraction of the diameter is nearly uniform over the whole length. As the extension proceeds, the local contraction (fig. 2) appears, and breakage ultimately occurs at the narrowest part of the neck.

Measurements taken from a large number of test-pieces show that the extensions can be represented as being due to (1) a general and uniform contraction of the diameter of the test-piece, and (2), in addition to this, a contraction of diameter, which at any given cross-section is a negative exponential function of the distance of that cross-section from the cross-section where the break occurs, the axis of the exponential curve being the generating line of the cylinder, to which the distant sections of the test-piece (had it been long) would have been reduced by (1).

The extensions corresponding to (1) and (2) will be considered separately.

Fig. 3.



Let $2l_0$ = original length of test-piece,

$2l_1$ = extended „ „

a_0 = original diameter „

a_1 = contracted diameter „

$E_1 = \frac{l_1-l_0}{l_1}$ = extension ratio reckoned on extended length,

$E_2 = \frac{l_1-l_0}{l_0} = \frac{E_1 l_1}{l_0}$ = „ „ original length,

B = force applied to produce breakage divided by original area of cross-section.

P = intrinsic strength of the material.

Taking first the extension corresponding to (1), since, as is well known, the density of the material is not appreciably affected by the extension,

$$l_0 a_0^2 = l_1 a_1^2, \quad \text{so that} \quad E_1 = (a_0^2 - a_1^2)/a_0^2.$$

Now

$$B = P a_1^2/a_0^2; \quad \text{thus} \quad B + 100E = P a_1^2/a_0^2 + 100 - 100 a_1^2/a_0^2. \qquad (I)$$

If the unit of force in which P is expressed is chosen so that P = 100 units and 100 units = 68 tons per square inch, $B + 100E_1 = 100$ units identically, if P is a constant. When E_1 is small, E_1 and E_2 are nearly equal, so that for small extensions

$$B + 100E_2 = 100 \text{ units nearly.}$$

For the extension corresponding to (2) take the axis of X parallel to the axis of the test-piece (4), and let x_2, x_3, be the abscissæ respectively of the broken end of the test-piece and the end (or mark) from which the extension is measured, and let y be the diameter at x.

The curve representing the diameter of the test-piece will be part of the curve $y = a(1-e^{-x/c})$, and the condition as to the constant density (*i.e.*, invariable volume of the material) gives the relation

$$\int_{x_2}^{x_3} y^2 dx = a_0^2 l_0.$$

Performing the integration, we have

$$\frac{x_3-x_2}{l_0} = 1+\frac{c}{l_0}\frac{y_3-y_2}{y_3}+\frac{c}{2l_0}\frac{y_3^2-y_2^2}{y_3^2}, \qquad \text{(II)}$$

$$E_2 = \frac{c}{l_0}\frac{y_3-y_2}{y_3}+\frac{c}{2l_0}\frac{y_3^2-y_2^2}{y_3^2}.$$

We may take y_3 as nearly equal to a_1, and if, for convenience, we put c equal to a_1, c being the value of x for which $(a_1-y)/a_1 = e$, then

$$B+100E_2 = Py_2^2/a_0^2+100\{(a_1-y_2)/l_0+(a_1^2-y_2^2)/2l_0a_1\}. \qquad \text{(III)}$$

To find the actual value of E by computation is laborious, but a simple graphical method can be employed (fig. 3).

We have on putting $l_0 = 1$, and $c = a_1$ in (II),

$$x_3-y_3-\tfrac{1}{2}y_3^2-1 = x_2-y_2-\tfrac{1}{2}y_2^2.$$

Drawing a curve for $y+\frac{1}{2}y^2 = z$, say, x_2 can be found for any assumed value of x_3 thus:—From x_3 subtract z_3+1, and through the point $x_3-(z_3+1)$ on the axis of x, and at an angle of 45° to the axis, draw a straight line to cut curve z in z_2, then the abscissa of z_2 is x_2.

In this way the diagram (fig. 4) has been constructed for test-pieces of the proportions which were used for measurement, viz. ($a = 0{\cdot}564$ inch, $2l_0 = 2$ inches).

An examination of this diagram shows how nearly constant the sum of the breaking stress and elongation per cent. is on the assumption that the intrinsic strength of the material is a quantity which is not altered by heat treatment, whether of hardening or annealing. It gives some evidence, however, that the intrinsic strength increases slightly as the material is extended, though not more than about 5 per cent. for an extension of 30 per cent.

The intrinsic strength of steel probably varies with the amount of carbon, but since Professor Ewing gives 60 to 70 tons per square inch as the average tensile strength of high carbon tempered steel, in which the extension must be small, the variation cannot be large.

Any considerable addition of nickel or chrome, however, seems to increase the intrinsic strength, as the same authority gives 90 tons as the breaking stress of a 12-per-cent. nickel steel and 80 tons for a chrome steel (percentage of chrome not stated).*

In saying that the intrinsic strength of all ordinary steels is about 70 tons per square inch, I exclude altogether the case of drawn wire or rolled plates, and refer only to such steel as is fairly isotropic and homogeneous at the

* "Strength of Materials," Ewing, 1906.

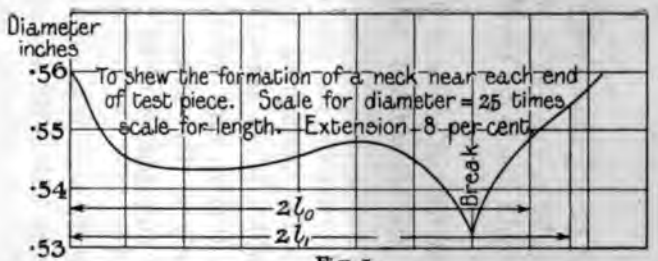

Diameter
inches
·56
·55
·54
·53
To shew the formation of a neck near each end of test piece. Scale for diameter = 25 times scale for length. Extension 8 per cent.
Break
$2l_0$
$2l_1$

Fig. 5.

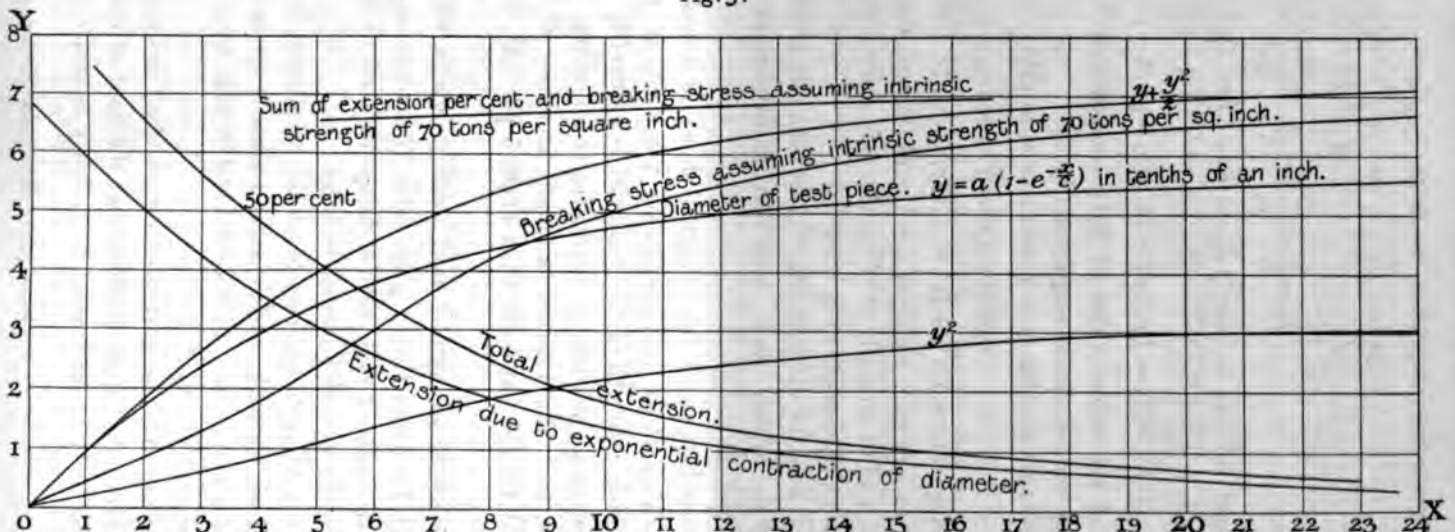

Y
X
Sum of extension per cent and breaking stress assuming intrinsic strength of 70 tons per square inch.
$y+\frac{y^2}{x}$
Breaking stress assuming intrinsic strength of 70 tons per sq. inch.
Diameter of test piece. $y=a(1-e^{-\frac{x}{c}})$ in tenths of an inch.
50 per cent
Total extension.
y^2
Extension due to exponential contraction of diameter.

Fig. 4.

commencement of the test. To compare the strength of a wire with the strength of the isotropic material is rather analogous to comparing the strength of a rope with strength of a felt made of the same fibre. The resistance of the rope to tension would be somewhat less than three times the resistance of the felt. The tensile strength of steel wire has been raised in some cases to more than twice the intrinsic strength of the material, but it is probable that, if the experiment could be tried, it would be found that the resistance to tension along a diameter of the wire was diminished.

When the condition regarding homogeneity and freedom from initial strain is fulfilled, I think the constancy of the sum of the breaking stress and extension per cent., and the approximation of this sum to 68, may be looked on as a good test of the quality and soundness of the steel.

If the sum is less than 68, it is an indication either of flaws or irregularities of structure, for it may be seen that the mere presence of parts having a different degree of ductility, without any actual flaws, would lessen the extension, because the less ductile parts would either give way first and so throw excessive stress on the rest, or if the harder parts did not extend with the rest the distortion of the neighbouring softer part would be excessive, and so cause a breakage.

It must be noted, however, that unsymmetrical holding of the test-piece in the testing machine would produce the same result, especially in the case of hard steels where the extension is small. See Nos. 14 to 19 and 21 to 23 in the Table, where the small extension is probably due, in part at any rate, to this cause.

It occasionally happens that the sum is greater than 68. This, I think, is due to the fact that what is called the breaking stress is the greatest stress measured, which is not always the stress at the moment of breakage. With very extensible steels the material at the neck gives way at the surface, while still holding on in the interior. Thus the working area at the moment of the break is somewhat less than the area of the broken surface, and the registered breaking stress in such cases refers to a period of the test before the extension has reached its ultimate value.

As far as I have observed the test-pieces rarely break in the middle of their length, and there is a tendency for a neck to be formed near both ends. Diagram 5 gives the results of some measures of diameter which show this. It is probably due to the sudden alteration in the diameter of the test-piece beyond the working part, which causes a non-uniform distribution of stress over the cross-sections in the neighbourhood. It should not appear in a test-piece where the diameter tapered gently to the working diameter.

A Table is appended giving the numerical results of some of the observations.

The general conclusion which I draw from the relations observed to hold between breaking stress extension and contraction of area, is that the various treatments and chemical compositions of ordinary mild steels (whether carbon nickel or nickel chrome), though operating powerfully on the limits of distortion, have but little effect on the intrinsic strength of the material.

Test-piece.	E.	B.	S.	D.	F.	Remarks.
1	30·5	39·0	69·5	0·419	71	F.
2	29·0	37·5	66·5	0·412	70	F.
3	29·0	41·0	70·0	0·438	68	N. F.
4	27·5	41·0	68·5	0·416	75	F.
5	26·0	42·5	68·5	0·432	72	L.
6	24·5	42·5	67·0	0·440	70	N. L.
7	24·0	42·5	66·5	0·450	67	L.
8	23·0	46·0	69·0	0·444	74	N. L.
9	22·6	46·0	68·6	0·430	78	F.
10	22·5	46·0	68·5	0·435	77	F.
11	21·0	45·0	66·0	0·440	75	L.
12	20·0	47·0	67·0	0·450	73	L.F.
13	20·0	47·0	67·0	0·440	77	L.F.
14	16·0	43·5	59·5	0·483	59	U.G. E. too small, B. too small.
15	15·0	43·5	58·5	0·496	56	U.G. E. „ B. „
16	15·0	44·0	59·0	0·480	61	U.G. (slightly), E. „ B. „
17	15·0	43·5	58·5	0·444	70	N.U.L. „ E. „ B. correct probably.
18	13·0	52·0	65·0	0·520	61	N.U.G. E. „ B. too small.
19	13·0	52·0	65·0	0·523	60	N.U.G. E. „ B. „
20	12·5	46·5	59·0	0·451	72	L.
21	10·0	50·3	60·3	0·534	56	U.G. (slightly), E. „ B. „
22	9·0	48·0	57·0	0·530	65	U.L. „ E. „ B. „
23	8·0	56·0	64·0	0·527	64	U.G. „ E. „ B. „

F. = fibrous fracture.
L. = laminated „
G. = granular „

E. = Extension per cent. on a length of 2 inches.

B. = Breaking stress in tons per square inch of original cross-section.

S. = Sum of breaking stress and extension.

D. = Measured diameter at break.

F. = Intensity of stress at broken surface (to the nearest ton per square inch) on the assumption that B. was the stress at the time breakage occurred.

N denotes nickel steel. U. means that the axis of the test-piece was bent, as well as extended. This may be due to the want of homogeneity, but is more probably the result of the test-piece not being held symmetrically in the testing machine.

An Examination of the Lighter Constituents of Air.

By JOSEPH EDWARD COATES, B.Sc. Wales.

(Communicated by Sir William Ramsay, F.R.S. Received November 29,—Read December 13, 1906.)

This research was undertaken with the object of ascertaining whether a large quantity of air, if systematically fractionated, would yield any constituent lighter than helium. It has been stated that "coronium" has revealed its presence in the gases emitted from the Solfatara of Pozzuoli by a line of wave-length 531·5—531·6; and that from some of the Vesuvian fumaroles gases have been obtained which give rise to new lines not coincident with any important lines in the neon or helium spectra.* Again, it has been stated by Dewar in a lecture delivered at the Royal Institution (April 11, 1902),† that in the most volatile part of the atmosphere "a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. The greater part of these rays are of, as yet, unknown origin."‡

A subsidiary object of the present research was to form a new estimate of the proportion of free hydrogen in air by the method of fractionation. The most important estimations have been made by Gautier, Rayleigh, and Dewar. Gautier, using the method of passing air over red-hot copper oxide, found 19·5 volumes of free hydrogen in 100,000 volumes of air, *i.e.*, about half as much free hydrogen as carbon dioxide.§ Rayleigh‖ discussed and, in part, repeated the work of Gautier; he considered three parts per 100,000 as a maximum estimate, but regarded the question as still unsettled. Dewar, in the lecture mentioned above, stated that "air contains as a minimum not more than $\frac{1}{100000}$th of free hydrogen."

The conclusions arrived at in this paper may be briefly stated: (1) there are no unknown lines in the spectrum of the lightest portions of the air, all those observed being traceable to helium, neon, and hydrogen; (2) the amount of hydrogen separable from air is much less than the maximum assigned by the above-mentioned investigators, for it amounts to about one volume per million and a-half volumes of air.

The first stage in the fractionation was effected by means of the air-

* Nasini, Anderlini, and Salvadori, 'Accad. dei Lincei,' 1898, vol. 7, pp. 73—74.

† 'Proc. R. Inst.,' vol. 17, p. 225.

‡ See also Dewar and Liveing, 'Roy. Soc. Proc.,' vol. 67, p. 467, 1900, "Spectrum of the More Volatile Gases of the Atmosphere Condensed at the Temperature of Liquid Hydrogen. Preliminary Notice."

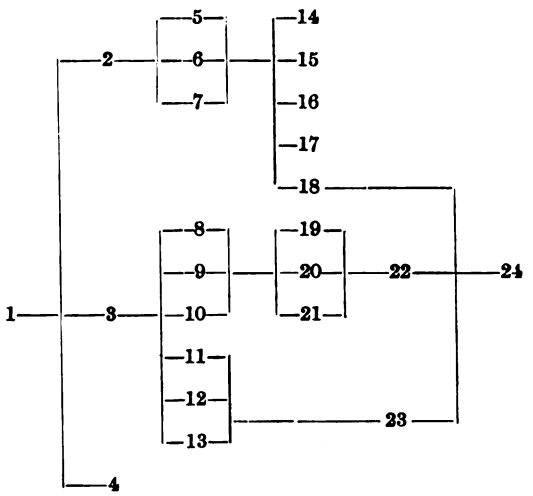
§ 'Ann. Chim. Phys.,' vol. 22, 1901.

‖ 'Phil. Mag.,' vol. 3, 1902, p. 416.

liquefying apparatus at University College, Gower Street. The air of the compressor room (situated in the basement and well ventilated) passed through the apparatus, and the portion which did not liquefy was collected in a large gas-holder. This, together with fresh supplies of air, was repeatedly circulated through the apparatus, with the object of making a preliminary concentration of the lighter portions. To avoid contamination with hydrogen, the gas-holder was well painted inside and the compressor cylinders lubricated with very dilute alkali. The total quantity of air dealt with in this operation amounted to about 73,500 litres.

A second fractionation of the gas thus collected was obtained by liquefying about 70 or 80 litres at a time in a glass bulb immersed in liquid air boiling under reduced pressure.* Light fractions were boiled off and the process repeated several times until the volume was reduced to 4700 c.c. This portion (1) was separated, by the method of absorption in cooled charcoal, into three fractions, (2) not absorbed at about $-190°$ C., (3) not absorbed at about $-110°$ C., (4) discarded. Spectroscopic examination showed (2) to be almost pure neon and helium with faint hydrogen lines. An attempt was made to fractionate (2) and (3) at the temperature of liquid air boiling at ordinary pressure ($-190°$ C.), but, in the case of (3), the fractions always showed the nitrogen spectrum (see table of fractionations); it was therefore decided to work at the temperature of liquid air boiling under reduced pressure, which represents a temperature of about $-205°$ C.

Table of Fractionations.



* A description of this piece of apparatus and its use has been given by Ramsay and ravers, 'Phil. Trans.,' A, vol. 197, 1901, p. 58.

Spectroscopic examination showed (5) and (6) to be chiefly neon and helium, with a little hydrogen—no new lines were detected; (7) was neon and nitrogen, while (8) and (11) consisted chiefly of nitrogen; (5), (6), (7) were mixed and separated into the fractions; (14) pumped off at −205° C., (15) at −190° C., (16) and (17) at 18° C., and (18) at 236° C.; (8), (9), (10) were mixed and similarly separated into fractions (19), (20), (21); (19) gave the nitrogen spectrum, (14) and (15) consisted of neon and helium; (16) and (17) contained hydrogen in addition to neon and helium, while (18) contained more nitrogen than neon. Fractions (14), (15), (16), (17) were therefore analysed for hydrogen, whilst the remaining fractions, as shown by the table, were worked up for neon and helium, of which 25 c.c. were obtained. The gases were measured separately, sparked with oxygen, the excess of which was subsequently withdrawn by means of phosphorus. The diminution in volume gave the amount of hydrogen present. The gases were measured by the method described by Ramsay.*

	c.c.		c.c.
Volume of (14).....	1·258	Volume of (15).....	1·995
„ after sparking	1·260	„ after sparking	2·001
„ of hydrogen...	nil	„ of hydrogen...	nil

N.B.—The slight increase in volume represents a small error of measurement of the order about 1 in 400.

	c.c.		c.c.
Volume of (16).....	11·615	Volume of (17).....	6·507
„ after sparking	11·420	„ after sparking	5·924
„ of hydrogen...	0·195	„ of hydrogen...	0·583

Total volume of hydrogen..... 0·778 c.c.

The spectra of (14), (15), (16), (17) were very carefully compared with the spectrum of a neon and helium tube, and they agreed exactly throughout; no new lines could be detected; this also shows that the contractions could not have been due to the presence of carbon monoxide, possibly derived from the charcoal. Any hydrocarbons in the air would have been removed in the charcoal.

As a test of this method of separating a small proportion of hydrogen from air, a parallel series of fractionations was performed on about 60 litres of air, to which 5·6 c.c. (measured to 0·1 c.c.) of hydrogen had been added. Three fractions were finally obtained from charcoal: (1) at −205° C., (2) and (3) at −190° C. Analysis, as before, gave the following results:—

* 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 113.

(1)	4·602 c.c.	gave	0·170 c.c.	hydrogen	(3·7 per cent.).
(2)	13·005	„	0·702	„	(5·4 „).
(3)	29·259	„	1·585	„	(5·4 „).
			Total volume of hydrogen.....		2·457 c.c.

Thus, only about half the added hydrogen was recovered. The most probable source of loss seems to be in the fractionation from the liquefied gas, when even the passage of air bubbles through the liquid appears insufficient to expel all the hydrogen. Dewar has also stated* that hydrogen is very soluble in liquid air; it is thus possible that a little hydrogen might have been removed during the initial process with the liquefying machine. It is noteworthy that the fraction pumped from the charcoal at −205° C. contains less hydrogen than that which comes off at −190° C.; the absorption of hydrogen seems to be of about the same order as that of neon.

The total volume of hydrogen obtained from the air was 0·778 c.c., and the total volume of mixed neon and helium was 46 c.c. Using the estimate of Ramsay,† agreeing with the previous one of Dewar,‡ viz., 60,000 volumes of air contain 1 volume of neon and helium together, it is found that 2,760,000 c.c. of air contain 46 c.c. of neon and helium and 0·778 c.c. of hydrogen, whence 3,550,000 c.c. of air contain 1 c.c. of hydrogen. This number can be corrected by assuming, as an approximate factor, the ratio 2·5/5·6 derived from the experiments on the air to which hydrogen had been introduced. The corrected estimate is 1 c.c. of hydrogen in 1,583,600 c.c. of air, or, approximately, one volume of hydrogen per million and a half volumes of air.

On comparing the total volume of air originally dealt with, it is evident that the liquefying plant was of very little use in concentrating the lightest portions; it is certainly better to calculate the hydrogen on the quantity of neon and helium actually obtained than on the original volume of air.

It appears from these results that the proportion of free hydrogen in the atmosphere is exceedingly small—so small, indeed, as to make its exact estimation a matter of extreme difficulty, and we must regard our results as indicating the order rather than the exact proportion in which the hydrogen is present.

In conclusion, I wish to express my warmest thanks to Sir William Ramsay, who suggested and constantly superintended the work during its progress.

* *Loc. cit.* † *Loc. cit.* ‡ *Loc. cit.*

The Photo-electric Fatigue of Zinc.

By H. STANLEY ALLEN, M.A., B.Sc., Senior Lecturer in Physics at King's College, London.

(Communicated by Professor H. A. Wilson, F.R.S. Received October 26,—Read November 15, 1906.)

Hertz's observation* that ultra-violet light can facilitate the passage of an electric spark led to the discovery of other photo-electric actions.† In the earliest experiments on the photo-electric effect of metals it was noticed that the action was diminished by exposure to light. Thus Hallwachs,‡ who found that a metal becomes positively electrified under the influence of ultra-violet light, states that "old surfaces no longer show the phenomenon. The radiation itself lowers the potential to which the plates can be electrified, so that with any succeeding experiment made with the same surface the potential obtained is lower, while the rise to it takes place more rapidly, and the decrease is greater than when for the same interval of time between the experiments the plate was not illuminated."

This diminution of the photo-electric action is spoken of as the "fatigue" of metals under the influence of light. It has received attention from many physicists, of whom Buisson§ and Ladenburg‖ may be specially referred to.

The present paper deals with the manner in which the photo-electric activity of zinc diminishes when the metal is exposed to light.

DESCRIPTION OF APPARATUS.

1. *Source of Light.*—Some preliminary experiments were made with the electric arc, limelight, and burning magnesium, but these proved too unsteady to give reliable results over long intervals of time, though the general character of the fatigue curves was similar to that of the curves obtained later with a steady source. A Nernst lamp was found to give enough actinic light for the observations, and when the current was supplied from a battery of large storage cells this source remained sufficiently steady for hours. When the lamp was run on the town mains the variations in voltage

* 'Wied. Ann.,' vol. 31, p. 983, 1887.

† See J. J. Thomson, 'Recent Researches' and 'Conduction of Electricity through Gases.'

‡ 'Phil. Mag.,' Series 5, vol. 26, p. 78, 1888.

§ 'Comptes Rendus,' vol. 130, p. 1298, 1900; 'Ann. Chim. Phys.,' vol. 24, pp. 320—398, November, 1901.

‖ 'Ann. d. Physik,' vol. 12, pp. 558—578, September, 1903.

of the supply caused considerable fluctuations in the current through the lamp and in the intensity of the light, as shown by corresponding irregularities in the fatigue curve.

2. *The Testing Vessel and Electrometer.*—The apparatus was practically a parallel-plate air condenser enclosed in a metal box. The construction of the testing vessel employed is shown in the diagram (fig. 1). The vessel was of brass, closed at top and bottom by brass covers screwed on. The top cover had a circular aperture closed by a quartz window, B. The central electrode, A, was insulated from the base by an ebonite plug, E. Small iron cups containing mercury are shown at D_1 and D_2, the latter being in metallic connection with the case of the apparatus, which was permanently earthed. A strip of copper supported by a wooden lever served to make or break the connection between the mercury cups, whilst the observer remained at a distance from the apparatus. C is a thick lead plate with a circular hole, placed between the light and the apparatus to shield the latter from ineffective radiation.

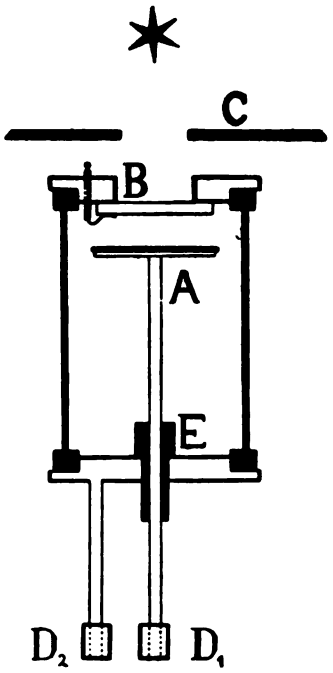


Fig. 1.

In most of these experiments the upper plate of the condenser was formed by the lower face of the quartz window, rendered conducting by phosphoric acid, as suggested by Strutt. In other experiments it consisted of a piece of wire gauze, supported by, but insulated from, the cover of the apparatus. This upper plate was connected to the positive terminal of a battery of small accumulators (200 elements), the other end of the battery being to earth. The lower plate of the condenser, formed by the piece of zinc to be tested, was connected to one set of quadrants of an electrometer, the other set being earthed. The rate of leak of electricity across the gap was measured by noting the time taken for the electrometer needle (observed with telescope and scale) to turn through a given angle. A Kelvin electrometer, with replenisher and gauge, was used most frequently, but in some experiments an electrometer of the Dolezalek type was employed.

3. *Method of Experimenting.*—The zinc plates used in these experiments were 5 cm. in diameter. They were either polished or amalgamated. In the former case the final polishing was done with rouge paper, either by hand or

in the lathe. Ladenburg* has pointed out that as the polish increases the discharge approaches a maximum, a result that was confirmed in these experiments. The surface of the amalgamated plate was renewed by rubbing a few globules of mercury over it with a cloth. The freshly polished or re-amalgamated plate was placed in the testing vessel, on the central electrode, the cover put in position, the electrical connections made and the Nernst lamp lighted. Observations were usually commenced within two minutes of the preparation of the plate and were continued as long as desired, readings of the rate of leak being generally taken at intervals of two minutes.

4. *Results of Experiments with Zinc.*—The general course of the decay curves was similar for polished and amalgamated zinc. The fatigue was very rapid immediately after exposing the metal to light, but after some time (usually 20 or 30 minutes from the commencement) the rate of decay became much slower. Such a result would be expected in the case of a change following the "compound interest law," but the initial decay observed compared with that in the later stages was even more rapid than would be required by such a change. The results are most clearly exhibited by plotting them on semi-logarithmic paper, where the ordinate represents the logarithm of the rate of leak, the abscissa the time from the first illumination of the plate. An exponential formula would be represented by a straight line. The curve representing the observed results consists of two parts, the first (AB) convex to the origin; the second (BC) a straight line inclined to the axes. That is to say, after about half an hour's exposure to light the decay of the activity may be expressed by a single exponential term. This was confirmed by continuing the observations over a long period.

The curve reproduced in fig. 2 shows that after the first rapid change the activity decays in an exponential manner for several hours.

The changes taking place during the first 100 minutes of the experiments are shown more clearly in figs. 3 and 4. The vertical scale in fig. 2 is not the same as in the later diagrams, for in these the rates of leak were about 10 times those recorded in the former figure. If the straight portion is continued backwards in the manner shown in fig. 2, and the difference between the rates of leak corresponding to P and P′ is plotted against the time on semi-logarithmic paper, another straight line is obtained, more steeply inclined to the horizontal axis. This shows that the experimental results can be represented by the sum of two exponential terms, so that the photo-electric activity is given by the empirical formula

$$I = K_1 e^{-\lambda_1 t} + K_2 e^{-\lambda_2 t}.$$

* *Loc. cit.*

For polished zinc this formula was found to apply under varied conditions, respecting the polish of the plate and the intensity of the illumination.

The value of λ_1 was more than 10 times that of λ_2, and K_1 was of the same order of magnitude as K_2.

5. In order to render more evident the agreement between the results of observation and those obtained by calculation from the above formula, the

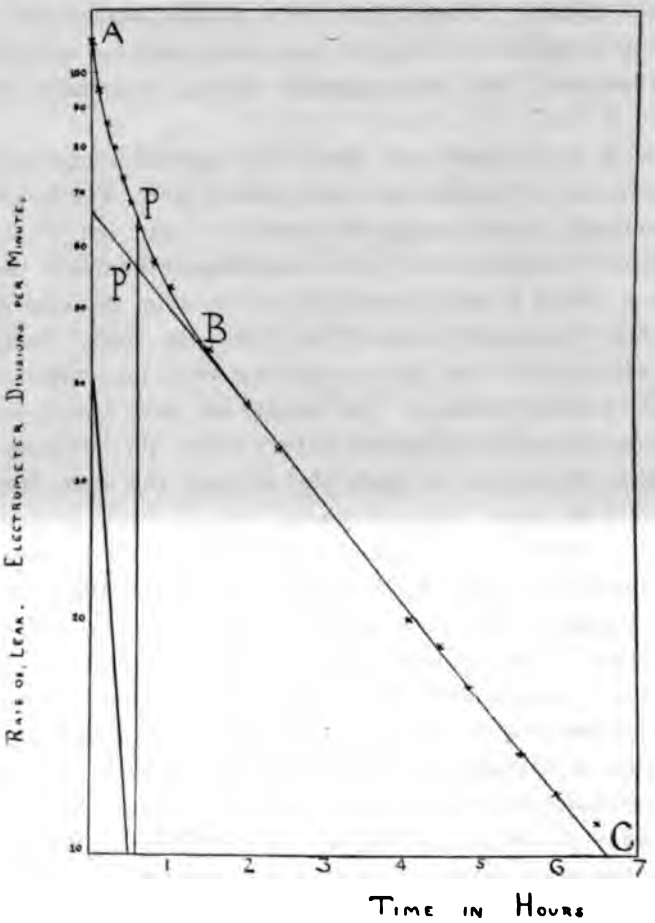


FIG. 2.

Photo-electric Fatigue of Zinc. Experiments made June 30, 1905. Nernst lamp taking 0·25 ampère on 110-volt circuit.

following table has been constructed for a selected case. This series of observations (August 7, 1905) was made with well polished zinc, illuminated by a 1-ampère Nernst lamp on a 110-volt circuit. The first reading was taken three minutes after the polishing of the zinc plate was completed. The exact instant of lighting the Nernst lamp was not noted in this experiment, but it

is assumed to have taken place two minutes after polishing. The first column of the table gives the time in minutes from the first illumination of the plate. The last column gives the observed value of the photo-electric current, expressed as the number of scale divisions that would be passed over in 100 seconds.*

Experiments made August 7, 1905, with well-polished Zinc Plate illuminated by Lamp. Nernst Lamp on 110 volt circuit.

t (mins.).	$K_1e^{-\lambda_1 t}$.	$K_2e^{-\lambda_2 t}$.	I (calc.).	I (obs.).
0	538	1153	1691	—
1	467	1144	1611	1611
3	352	1128	1480	1427
5	266	1111	1377	1349
7	200	1095	1295	1280
9	151	1079	1230	1217
11	114	1063	1177	1174
13	86	1048	1134	1134
15	65	1032	1097	1096
17	49	1017	1066	1085
19	37	1003	1040	1040
21	28	988	1016	998
23	21	973	994	988
25	15	959	974	969
27	12	946	958	941
29	9	931	940	933
31	7	917	924	915
33	5	904	909	907
35	4	890	894	891
37	3	878	881	891
39	2	865	867	853
41	2	852	854	845
43	1	839	840	845

t (mins.).	I (calc.).	I (obs.).	t (mins.).	I (calc.).	I (obs.).
45	827	824	73	673	665
47	815	824	75	663	665
49	804	811	77	654	647
51	792	804	79	644	639
53	780	767	81	635	623
55	769	779	83	625	608
57	758	755	85	616	617
59	747	750	87	607	602
61	736	750	89	598	594
63	725	739	91	590	591
65	714	717	93	581	587
67	704	717	95	573	570
69	694	697	97	564	554
71	683	683	99	556	554

* The actual observation was the time taken to pass over 100 scale divisions. One division per second corresponded to $0{\cdot}48 \times 10^{-12}$ ampère.

In the fourth column we have the calculated value of the current, the number being the sum of those in the two preceding columns. The first exponential term falls to half value in 4·9 minutes, the second in 94 minutes, the constants of change being $\lambda_1 = 0{\cdot}141$ and $\lambda_2 = 0{\cdot}00737$. The first term accordingly diminishes in value rapidly and becomes inappreciable after

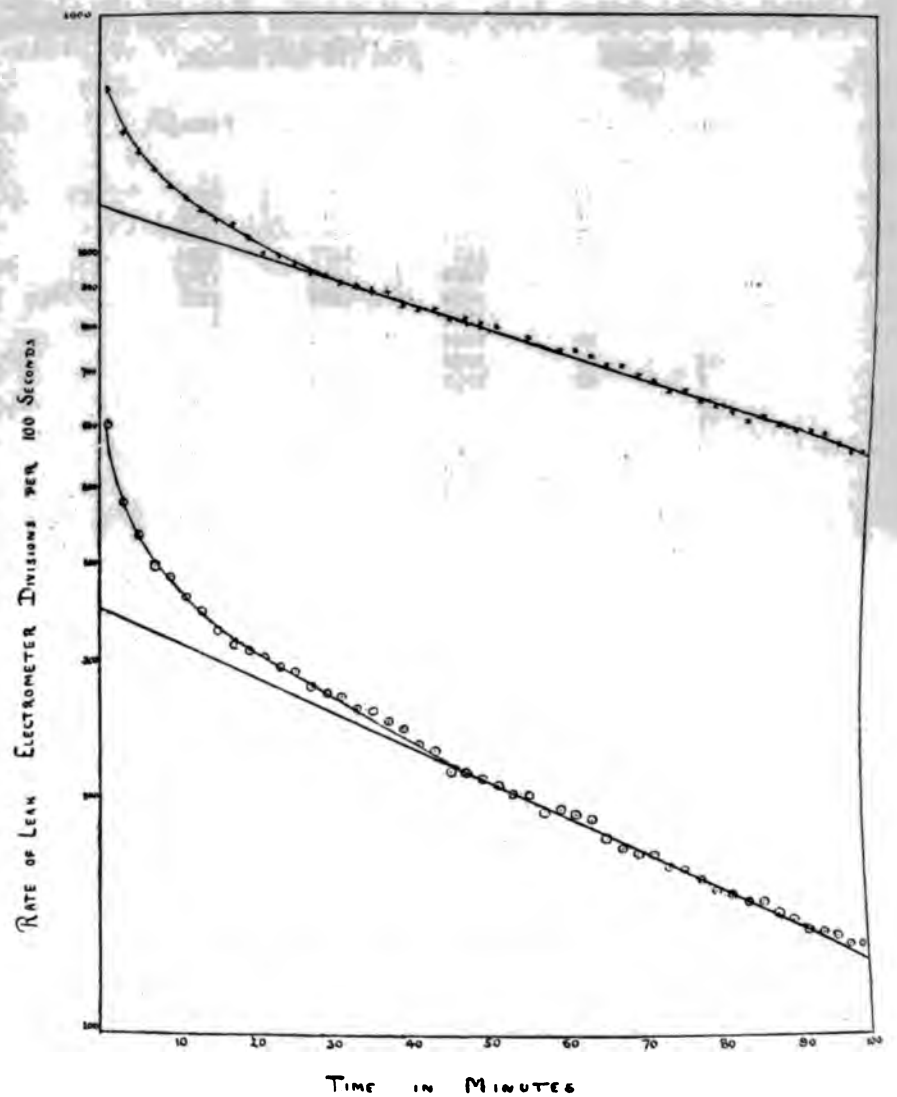


FIG. 3.

Photo-electric Fatigue of Zinc.

× Experiment made August 7, 1905, with well-polished zinc.

⊙ Experiment made July 24, 1905, with polished zinc. Nernst lamp taking 1 ampère on 110-volt circuit.

45 minutes. The values for the calculated current in the second part of the table are derived from the term $K_2e^{-\lambda_2 t}$.

6. These results are plotted on semi-logarithmic paper in fig. 3. On the same diagram is shown the fatigue curve for another experiment (July 24, 1905), in which the zinc plate was polished by hand instead of in the lathe, giving much smaller values for the photo-electric current. The constants of change in this case are $\lambda_1 = 0{\cdot}1365$ and $\lambda_2 = 0{\cdot}0104$, the time taken to fall to half value being 5 minutes and 67 minutes respectively.

7. The values found for λ_1 and λ_2 were of the same order as those just mentioned, in all the experiments carried out with polished zinc, although the conditions as to polish and to intensity of illumination were varied within wide limits. The rate at which the character of the surface changes under the influence of light is consequently not much affected by the conditions named.

8. *Results of Experiments with Amalgamated Zinc.*—Fatigue curves of a similar character were obtained with amalgamated zinc. One of the curves is shown in the lower half of fig. 4. In the rapid change at the outset the activity falls to half value in 4·2 minutes, the constant of change being $\lambda_1 = 0{\cdot}164$. The second change is much slower, the time taken for the activity to diminish one half being 167 minutes and the value of λ_2 being 0·00414. In this case K_1 is 854 and K_2 is 148 (scale divisions per 100 seconds), so that K_1 is about six times K_2.

9. The experiments I have carried out, using the Nernst lamp as a source of light, confirm in most particulars the results arrived at by Buisson* with sunlight. The chief point of difference is the clear recognition of the fact that the rate of decay at the outset is too great to be represented by the single exponential that is sufficient for the later stages. This is, in fact, mentioned by Buisson, but is attributed to experimental errors consequent upon the use of a gold-leaf electroscope. I have plotted some of his results, and find that they can be represented with far greater accuracy by employing two exponential terms.

10. *Theory of Successive Changes.*—The experiments already described show that the photo-electric activity of a zinc plate decays in a perfectly definite manner when a freshly-polished plate is exposed to light. The activity at any time t after the plate has been polished can be represented by an empirical formula containing the sum of two exponential terms,

$$I = K_1e^{-\lambda_1 t} + K_2e^{-\lambda_2 t}.$$

* *Loc. cit.*

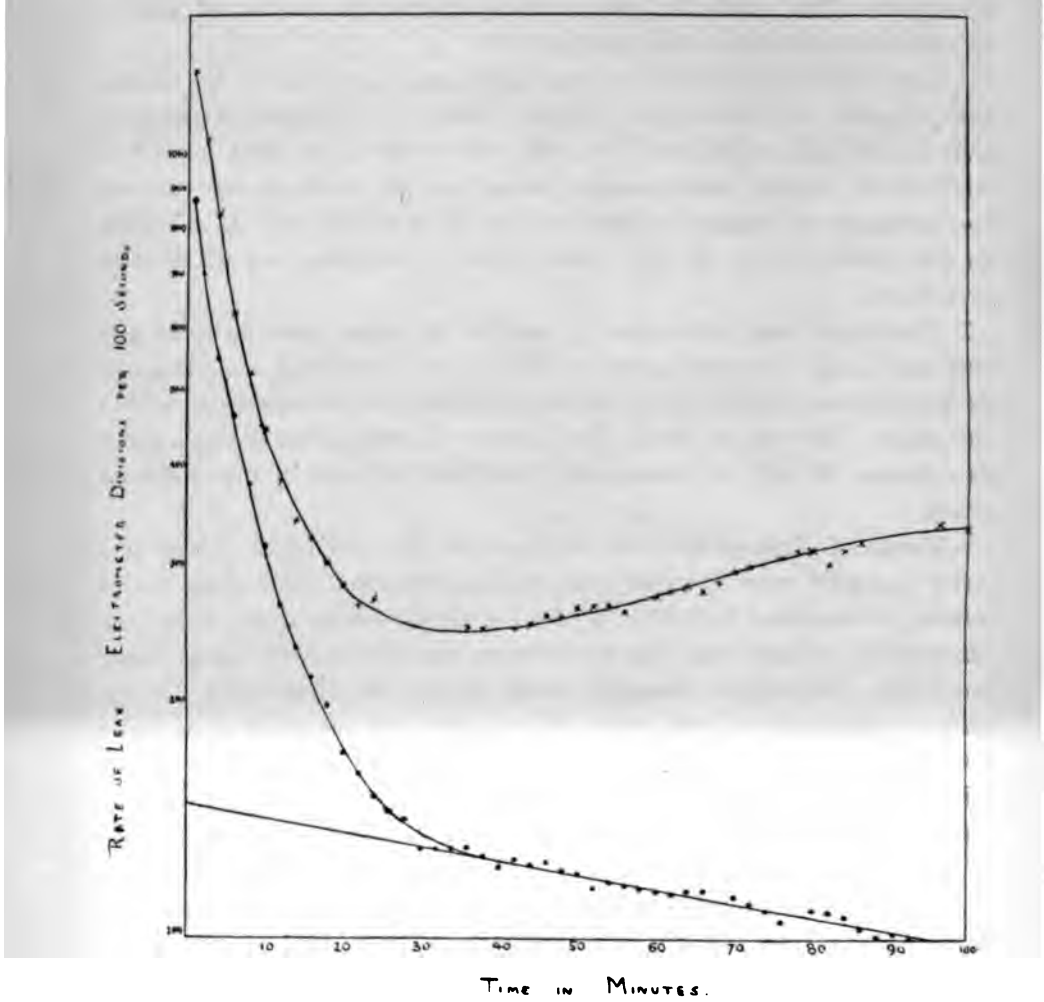


FIG. 4.

Photo-electric Fatigue of Amalgamated Zinc.

× Experiment made July 28, 1906, without absorbing solution.

● Experiment made August 1, 1906, with absorbing solution. Nernst lamp taking 1 ampère on 110-volt circuit.

To explain this result we assume that freshly-polished zinc (A) gives out negative ions under the influence of ultra-violet light, and changes to a form B (the change may be either a physical or a chemical one). B also gives rise to a supply of negative ions, and changes to a third form, C, which is supposed to be inactive.

At present we do not consider the nature of the substances (whether physical or chemical modifications of zinc) denoted by B and C.

Suppose we start with a quantity a of substance A. Let this change into B in such a way that the rate of change at any instant is proportional to the quantity still unchanged. Let B subsequently change into C, in accordance with the same law. If x, y, z denote the quantities of the several substances present at a time t,

$$x+y+z=a.$$

For the change from A to B

$$-\frac{dx}{dt}=\lambda_1 x, \quad \text{so} \quad x=ae^{-\lambda_1 t}.$$

The quantity λ_1 is the "velocity coefficient" of the first change.

The rate at which B accumulates is equal to the quantity supplied by A, less the quantity that changes into C, thus—

$$\frac{dy}{dt}=\lambda_1 x-\lambda_2 y,$$

λ_2 being the velocity coefficient for the second change.

This gives

$$\frac{dy}{dt}+\lambda_2 y=a\lambda_1 e^{-\lambda_1 t}.$$

To solve this equation we assume

$$y=De^{-\lambda_1 t}+Ee^{-\lambda_2 t}.$$

Substituting this value, we find

$$-D\lambda_1+D\lambda_2=a\lambda_1, \quad \text{or} \quad D=-\frac{a\lambda_1}{\lambda_1-\lambda_2}.$$

When $t=0$, $y=0$; so $E=-D$, giving

$$y=\frac{a\lambda_1}{\lambda_1-\lambda_2}(e^{-\lambda_2 t}-e^{-\lambda_1 t}).$$

Thus, finally, we obtain as the values* of x, y, and z,

$$x=ae^{-\lambda_1 t},$$

$$y=\frac{a\lambda_1}{\lambda_1-\lambda_2}(e^{-\lambda_2 t}-e^{-\lambda_1 t}),$$

$$z=a\left(1+\frac{\lambda_2}{\lambda_1-\lambda_2}e^{-\lambda_1 t}-\frac{\lambda_1}{\lambda_1-\lambda_2}e^{-\lambda_2 t}\right).$$

We assume that the observed photo-electrical activity is due in part to the substance A, in part to the substance B, so that we write

$$\frac{I}{I_0}=\frac{Ax+By}{Aa},$$

where A and B are constants measuring the activity of the corresponding substances.

* These results are given in Rutherford's 'Radio-activity' (Second Edition, § 197).

Substituting for x and y we obtain

$$\frac{I}{I_0} = \left(1 - \frac{B}{A}\frac{\lambda_1}{\lambda_1 - \lambda_2}\right) e^{-\lambda_1 t} + \frac{B}{A}\frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_1 t}.$$

This expression is of the required form, provided the coefficients are both positive quantities, for the empirical results can be represented by the sum of two exponential terms.

To satisfy this condition λ_1 must be greater than λ_2, *i.e.*, the first change must be the more rapid one.

In the experiments already described λ_1 was large in comparison with λ_2, so that an approximate value of the activity is given by

$$\frac{I}{I_0} = \left(1 - \frac{B}{A}\right) e^{-\lambda_1 t} + \frac{B}{A} e^{-\lambda_2 t}.$$

As K_1 is of the same order of magnitude as K_2 for zinc, we should require to make A approximately twice as great as B.

11. *Recovery Due to the Longer Light Waves.*—In some of the experiments, more particularly with amalgamated zinc, the rapid fatigue at first observed was followed by a gradual recovery of the activity to a maximum value, which was, however, far smaller than the initial value. After this maximum value was passed the ordinary slow decay set in. This effect is illustrated in the upper curve of fig. 4, which shows the first part of the fatigue curve with the sudden fall in activity at the start followed by a gradual rise. The subsequent slow decay is not shown here.

The small recovery observed in these cases was traced to the action of the longer waves from the Nernst lamp. It was very much diminished by filling the cell in the cover of the testing vessel with water and was completely eliminated when the water was replaced by a solution of alum. The fatigue curve obtained with amalgamated zinc when the longer waves are absorbed is shown at the bottom of the same figure.

This action of the waves of greater wave length may be due simply to a temperature effect, for the photo-electric activity of metals is in general greater at a high temperature than at a low one; or it may be analogous to the effect observed by Buisson,* who found that all radiations do not work in the same sense as regards the contact difference of potential.

12. *Experiments on Zinc in a Vacuum.*—Ladenburg† has shown that many metals exhibit photo-electric fatigue in a vacuum. Buisson‡ also maintains that the alteration in a metallic surface produced by sunlight is independent of the pressure. On the other hand, Varley§ states that zinc illuminated by the light of an iron arc shows little or no sign of fatigue when the pressure

* *Loc. cit.* † *Loc. cit.* ‡ *Loc. cit.*

§ 'Phil. Trans.,' pp. 439—458, 1903.

is below, say, the tenth of an atmosphere. Smolochowski, in some unpublished experiments on the liquid alloy of sodium and potassium, found that the decay phenomena do not take place in a high vacuum.

I have carried out some experiments on zinc in a good vacuum obtained by Dewar's method of absorbing the gas by charcoal cooled in liquid air, and found that the light of a Nernst lamp produced unmistakable fatigue. The results, however, were not sufficiently accurate to allow satisfactory fatigue curves to be drawn.

13. *Summary and Conclusion.*—The experiments described in this paper show that it is necessary to employ the sum of two exponential terms in order to obtain an adequate representation for the photo-electric fatigue curve of zinc. Just as Rutherford has explained the curves of decay for the excited activity of radium and thorium as a consequence of successive changes, so it is possible to explain the present results as due to two consecutive changes. The nature of the modifications thus suggested is left an open question.

It is also shown that the longer waves of light can bring about a change in the opposite sense, that is to say, they can produce a certain amount of recovery of photo-electric activity.

In conclusion, I must express my great indebtedness to Lord Blythswood, in whose laboratory at Renfrew some of these experiments were carried out, and also to Professor H. A. Wilson for advice and suggestions during the period of my work in the Wheatstone Laboratory of King's College, London.

[*Note added October* 9.—In a paper published in the 'Philosophical Magazine' for the present month (pp. 414—418), Sir Wm. Ramsay and Dr. Spencer discuss the "tiring" of metals when exposed to ultra-violet light. The curves they have obtained for magnesium, zinc and tin show a number of breaks, the number corresponding to the number of valencies of the metal. In the case of aluminium at least five or six breaks were observed. The fatigue curves that I have obtained for zinc illuminated by the light of a Nernst lamp do not show these breaks,* unless the point at which the first rapid change becomes insensible is regarded as a break in the curve.

If the results given above are interpreted in terms of the theory put forward by Sir Wm. Ramsay and Dr. Spencer, the modification that I have called zinc B would presumably correspond to zinc which has lost the first of the "metallic corpuscles."]

* This may, perhaps, be due to the fact that the same zinc plate was used repeatedly, being repolished before an experiment. According to Sir William Ramsay and Dr. Spencer, the breaks in the curve are much less persistent in such a case.

The Effect of Temperature on the Activity of Radium and its Transformation Products.

By HOWARD L. BRONSON, Ph.D.

(Communicated by Professor E. Rutherford, F.R.S. Received November 3,—Read November 15, 1906.)

Introduction.

A large number of investigators have attempted to alter the activity of various radio-active substances by subjecting them to very high and also to very low temperatures. Among all these attempts only two, as far as the writer is aware, have apparently given positive results.

Curie and Danne* found that the rate of transformation of the active deposit from radium was apparently permanently increased after it had been subjected to temperatures above 800° C. The writer† repeated these experiments, and showed that this apparent increase was due to the volatilisation of radium B. By having the active deposit sealed in a glass tube when heated, it was shown conclusively that the rate of transformation had not been permanently altered by temperature up to 1100° C. In both the above experiments the rate of transformation was determined in the cold after the active matter had been removed from the furnace, and no attempt was made to detect any change in the activity of the active deposit while it was actually at a high temperature.

Results Obtained by Makower.

Makower‡ has more recently made some further investigations on the same subject. He concludes: "The results show clearly that the activity, as measured by the β and γ rays, can be changed by high temperatures, the observed effects being *consistent* with the explanation offered by Curie and Danne, that the rate of decay of radium C is increased by high temperatures." The method employed by Makower differed from that employed in the previous experiments, in that he subjected radium emanation (which was in a state of radio-active equilibrium) to the high temperature, instead of merely the active deposit. The emanation was sealed in a quartz tube so that no volatile product could escape. This method had this advantage, that although the measurements were also taken when the tube was cold,

* 'Comptes Rendus,' vol. 138, p. 748, 1904.

† 'Amer. Journ. Sci.,' July, 1905, and 'Phil. Mag.,' Jan., 1906.

‡ 'Roy. Soc. Proc.,' March, 1906.

yet it was possible to detect changes in the activity which had occurred during the time of heating. The activity of the quartz tube was always found to be diminished after it had been heated to 1000° C. or over. The amount of decrease varied from 3 to 15 per cent., depending on the temperature and length of time of heating. On account of the presence of the emanation, the activity recovered its normal value again after about one hour, apparently showing that, after heating, the rate of production of the active deposit was greater than the rate of decay. No light, however, was thrown on the question, investigated by Curie and Danne and the writer, as to whether the rate of decay of the active deposit had been *permanently* altered or not.

The arrangement of the apparatus employed by Makower is shown in fig. 1. The ionisation in the testing vessel was produced by both β and γ

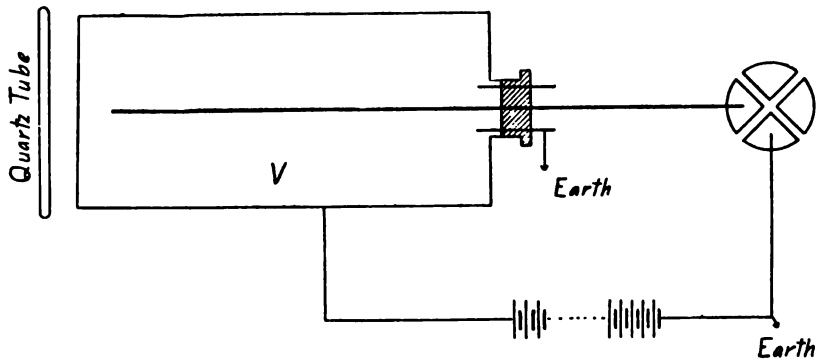


FIG. 1.

rays, and it is easily seen that the distribution of the active deposit in the quartz tube might have considerable effect on the observed activity. It is also to be noticed that no change in the activity took place until a temperature of about 1000° C. was reached, which is about the temperature at which radium C begins to volatilise.

As all the results obtained by Makower can be satisfactorily explained on the assumption that radium C volatilised and deposited itself near the ends of the tube, it seemed desirable to further test the effect of high temperatures on the activity of radium and its transformation products under quite different experimental conditions.

Apparatus and Method.

The arrangement of the apparatus, as used in the following experiment, is shown in fig. 2. A few tenths of a milligramme of pure radium bromide

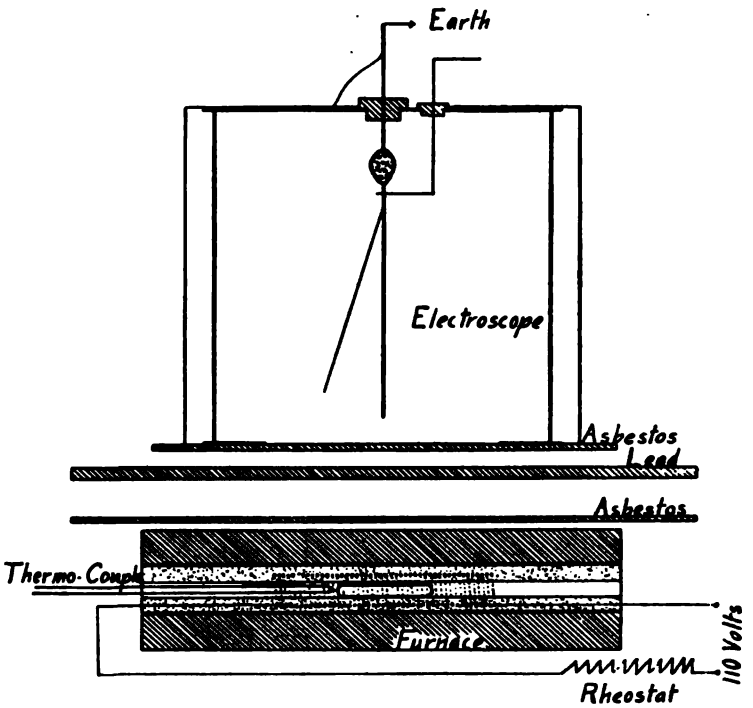


FIG. 2.

was sealed in a quartz tube, under diminished pressure, and placed in a small electric furnace directly below the electroscope, as shown in the figure. In order to protect the electroscope from convection currents of air, it was entirely surrounded by another vessel and separated from the furnace by two layers of asbestos and one of lead, with air spaces between them. In addition to this, the air between the furnace and the electroscope was continuously removed by an electric fan, not shown in the figure. Even with these precautions the gold leaf did not move with perfect regularity, but the errors due to this fact were very small, as can be seen from the observations plotted in fig. 3 (see p. 499).

After several unsuccessful attempts, a satisfactory platinum resistance furnace was constructed, with which a temperature above 1600° C. was obtained. The construction of the furnace is shown in the figure. The inside cylinder was a platinum tube, which was surrounded by a layer of magnesium oxide in which the platinum wire was embedded. Surrounding the magnesium oxide was a porcelain tube, which in turn was covered with a thick layer of asbestos.

The temperature was measured by a platinum-rhodium thermo-couple, and

a potentiometer specially designed for such measurements by Professor H. M. Tory. The couple was calibrated up to 1100° by comparison with one of Dr. Barnes' platinum resistance thermometers, which had been carefully standardised. The calibration curve was extended beyond 1100° by means of an equation given by Le Chatelier. This equation is of the form $\log e = a \log t + b$, where e is expressed in micro-volts. This equation with suitable constants fitted the calibration curve almost perfectly below 1100°. In order to make certain that it held true for higher temperatures, the melting point of platinum was directly determined, and was found to differ from the calculated value by less than 10°.

The relative position of the quartz tube and thermo-couple in the furnace is shown in the figure. It is easily seen that the temperature of the couple is certainly not higher than that of the quartz tube. It is therefore evident that the values given for the temperatures in this paper are certainly not too high.

The arrangement of the apparatus as described above furnishes certain favourable experimental conditions to which attention should be called. Errors due to change in the distribution of radium C were largely avoided by making the quartz tube short (about 4 cm.), in comparison with the diameter of the electroscope (about 12 cm.), and by measuring the activity entirely by the γ rays. Any possible error introduced by the decay of the emanation was avoided by the use of radium itself as the active substance. The relative position of the quartz tube and the electroscope remained absolutely unchanged throughout the entire experiment. The *great* advantage, however, of the above arrangement lay in the fact that measurements of activity and temperature could be taken simultaneously. This made it possible instantly to detect any change in the activity of radium C, as its temperature was raised.

The importance of this point becomes evident, when we consider the complexity of the problem under investigation. This complexity arises from the fact that there were five radio-active substances in equilibrium, sealed together in the quartz tube. Since the writer has shown that the rate of transformation of the active deposit is not permanently altered by subjecting it to temperatures up to 1100° C., the only explanation of the decrease of activity observed by Makower is that the equilibrium quantity of radium C at high temperatures is less than normal. A number of special cases will perhaps make this point more evident.

For simplicity we will assume that in any particular case only one of the active substances is affected by the temperature. For example, suppose that at a certain definite temperature the rate of transformation of radium C is

suddenly increased, the electroscope will show a sudden increase in the activity. This increase in activity will not be permanent, but will gradually diminish and practically disappear after three hours. This follows from the fact that, when equilibrium is reached, the number of atoms of radium C which break up per second must be the same as the number supplied, and this number, according to our assumption, has not been changed. If now after equilibrium is reached at this temperature the active matter is removed from the furnace and its activity measured again at ordinary temperature, it will be found to be less than normal, since the number of atoms of radium C present is less than the normal number. As a second example, suppose that the rate of transformation of radium B is suddenly increased. At once the activity of radium C begins to rise, reaches a maximum in about 35 minutes, and decays to its normal value again in about three hours. An increase in the rate of transformation of the emanation would produce similar results, except that it would take about three hours for the activity of radium C to reach a maximum, and as much as three or four weeks to decay to its normal value again. With radium A the case is quite different. Its rate of transformation is so rapid that it would regain its equilibrium value very quickly. Therefore, unless a very large change in its rate of transformation took place, the effect on the activity of radium C would be very small and difficult to detect. On the other hand, the rate of transformation of the emanation is so slow, that any change in the activity of radium would not appreciably affect the activity of radium C for several hours, and could not possibly be detected in the present experiment. The above discussion is all based on the assumption that the activity is being measured by the penetrating γ rays, which come entirely from radium C.

It is thus clearly seen not only that it should be possible to determine the effect of high temperatures on the activity of the emanation and the active deposit, but that the particular substances affected ought also to be determined by the way in which the activity, as measured by the γ rays, changes.

Observations.

When the apparatus was once arranged, as explained above, it was a very short, simple operation to perform the experiment. Simultaneous observations of activity and temperature were taken at intervals of two or three minutes. The temperature of the furnace was raised gradually up to about 1300° C. It was allowed to remain between this temperature and 1350° for over an hour, and then gradually raised again to 1500°. After keeping it at about this temperature for nearly another hour, it was raised again to over 1600°.

At about this temperature two difficulties were encountered, the insulation of the furnace failed, and the emanation began to escape from the quartz tube. The slightly increased activity shown by the last observation (fig. 3) was due to this escape of the emanation and its presence around the electroscope. The furnace was then allowed to cool. Its activity measured several hours later was found to be less than half its original value. That this decrease in activity was actually due to the escape of the emanation was shown by the fact that the quartz tube regained about half its lost activity during the next four days.

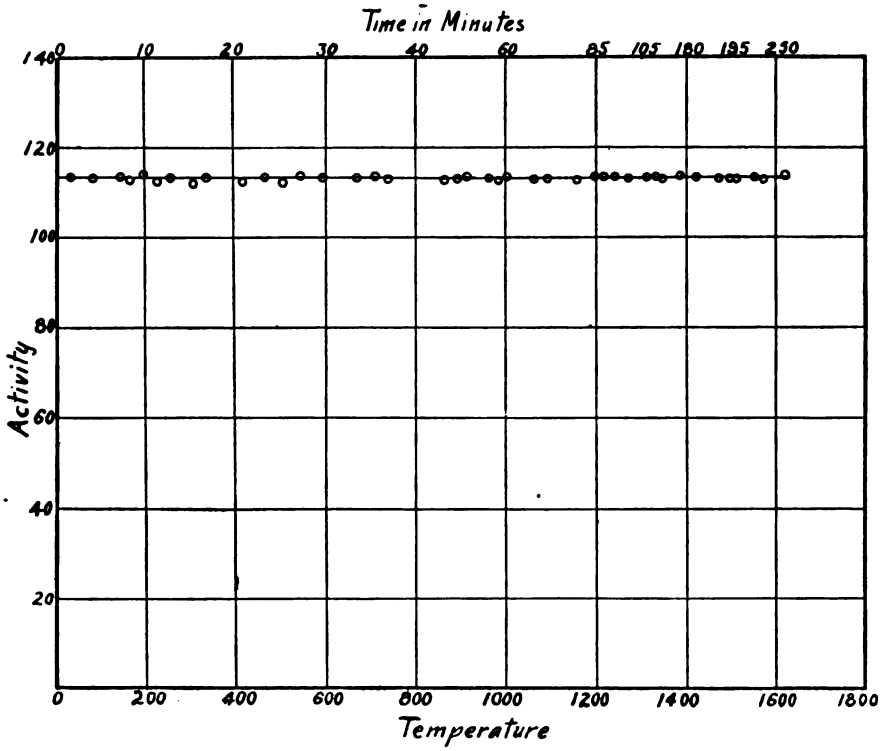


FIG. 3.

Fig. 3 shows the results of the series of observations above described. The approximate times at which the measurements were taken are given at the top of the figure. Below 1200° each point in general represents a single observation, while above this temperature most of them represent a mean of several, which accounts for their greater regularity. There is no evidence of any change in the activity as measured by the penetrating γ rays. If any change at all took place, it was certainly less than 1 per cent.

The length of time during which the temperature of the furnace was above

1500° was sufficient to have made it possible to detect a 1-per-cent. variation in the rate of transformation of either the emanation or radium B, but there was no evidence of any such change. A similar set of observations taken with decreasing temperatures also failed to reveal any change in the activity.

Effect of Low Temperature.

A number of investigators have tried the effect of subjecting radium to low temperatures, and have obtained negative results in every case. Nevertheless, it seemed worth while to supplement the above experiment by trying the effect of low temperature on the same radium that had been previously heated. Only one temperature was tried, namely, that of liquid air. The quartz tube was hung in a Dewar bulb beside the electroscope and its activity measured. The bulb was then filled with liquid air and measurements taken continuously for an hour, but there was no evidence of any change in the activity.

Conclusions.

The above experiments show no evidence whatever of any change in the activity of the transformation products of radium, when they are subjected to temperatures between −180° and 1600° C. If any change does take place, it is very small, and cannot be over 1 per cent. in the case of radium C for temperatures between −180° and 1600°, nor more than 1 per cent. in the case of the emanation of radium B for temperatures between −180° and 1500°.

There is thus removed the only known exception to the general rule, that the activity of radio-active substances is not affected by temperature.

In conclusion, I take pleasure in expressing my thanks to Professor Rutherford, who suggested the subject, and furnished all the necessary material for the investigation.

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OF

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JOHANNES WISLICENUS. 1835—1902.

THERE are few branches of science so indelibly associated with the second half of the last century as that highly-specialised study of the compounds of carbon, which is commonly called organic chemistry. The marvellously rapid development of this branch of chemistry will ever remain one of the greatest monuments to the enthusiasm and industry of scientific workers. Amongst the master-builders of this imposing edifice, one of the most conspicuous was Johannes Wislicenus, who, over a period of more than forty years, devoted his great natural gifts and extraordinary energy to this work of construction.

J. Wislicenus

(about 1875).

Although in 1853, at the early age of 18, we already find Wislicenus acting as assistant to Heintz, then Professor of Chemistry in the University of Halle, his further progress to academic distinction did not proceed on the stereotyped lines usually followed by those who succeed in gaining access to the select professorial caste of the German universities. Wislicenus' early life is, in fact, of special interest, taking us back as it does to a time when liberty and freedom of speech were ideals for which serious sacrifices had to be made even in the countries of Western Europe.

Wislicenus was born on June 24, 1835, at Kleineichstad in Saxony, of which village his father, Gustav Adolf Wislicenus, was the pastor. He came of one of those stocks which betray their independent spirit and originality by finding themselves out of sympathy with the established religion of their fellow-countrymen, for the Wislicenus family, originally Polish, had, in consequence of their Protestant zeal, been forced to fly from Poland into Hungary, from where, in the 17th century, they passed into Germany. For several generations members of the family were engaged in the ministry at

Schönburg, near Naumburg. The inherited capacity of suffering for conscience sake, however, was again manifested in Wislicenus' father, who, in consequence of belonging to a students' society ("Burschenschaft") for the promotion of liberal principles, was, in 1824, condemned to twelve years' imprisonment in a fortress, but was pardoned after suffering confinement for five years. Far from being crushed by this cruel punishment, he was again in 1844 identified with resistance to the persecution carried on by the orthodox party under William IV of Prussia, and for his liberal preaching he was in 1846 deprived of his living as pastor in Halle. He at once founded a free church in the same city, but was in 1853 condemned to two years' imprisonment for publishing a work entitled "The Bible in the Light of the Culture of our Time," to escape which he was obliged to fly to America. It would, indeed, be difficult to find a more ideal ancestry for a man of science!—a line of forefathers in whom two hundred years of exile and persecution had been unable to extinguish the innate love of truth and heroic devotion to the cause of free thought.

Through his father's flight to America, Johannes Wislicenus' studies at the University of Halle had to be interrupted at the age of 18, for it was under his guidance that the family followed the father to the New World. Owing to limited resources they were obliged to set out across the Atlantic in a sailing ship, on which they embarked in England, but hardly had they got under way before cholera broke out on board, and the disease spread with such rapidity that the state of affairs soon became most serious. The writer well remembers the graphic description given him by Wislicenus of the scenes which ensued. The doctor, a Scotchman, proved himself wholly incapable of grappling with the situation; he entirely neglected the steerage passengers, and had recourse to the whisky bottle. Young Wislicenus thereupon undertook not only the treatment but even the nursing of the wretched patients who had been left to their fate by the medical officer. The pestilence, however, assumed such dimensions that the ship was turned back to England, and the voyage abandoned. Owing to the family being provided with money but barely sufficient to carry them to America, the enforced delay in England entailed on them much hardship and suffering, and the bitter experiences of this dark time must have so impressed themselves on the youthful Wislicenus that it was not until thirty-four years later that he could be induced to revisit this country, notwithstanding the reiterated invitations of his many English friends.

On ultimately reaching the United States it was again to Wislicenus, but little more than a boy in years, that the family looked for material support. He became assistant to Professor Horsford, of Harvard, and subsequently carried on practice as an analytical chemist in New York. Wislicenus used to relate many interesting episodes of his three years' life in the States. On one occasion, as he told the writer, he was visited in his laboratory by two Americans, who requested him to analyse and report on a sample of water from a mineral spring which they wished to push for its therapeutic

properties. They said they must have the analysis and report by the afternoon of the same day. This, said Wislicenus, was quite impossible, as the analysis would certainly take several days, and possibly longer. His visitors replied that they would, of course, be prepared to pay him more than the usual fee, but that the results of analysis must be in their hands by the afternoon. Their surprise was unbounded when Wislicenus declined to oblige them, and, saying that they guessed he must be a young greenhorn, they went to another chemist of high repute in the city, who duly furnished them with an elaborate analysis and report in the course of a few hours. This chemist subsequently informed Wislicenus, quite cynically, that, to meet the exigencies of the case, he had devised a method of analysing water by smell! In such an atmosphere Wislicenus began to feel doubts as to his moral security, and he formed the resolve of returning to Europe as soon as he possibly could.

In 1856 the family recrossed the Atlantic and settled in Zürich, where Wislicenus resumed his studies, and in the following year became private assistant to his former master, Professor Heintz, at Halle. Here he remained until 1859, taking his Ph.D. degree in 1858 on an investigation which he had made of the basic decomposition products obtained by heating aldehyde-ammonia. This, and several other pieces of work, were published in conjunction with Heintz, whilst Wislicenus' first independent papers appeared in 1859 and treated of the theory of "mixed types," with special reference to the derivatives of glycerine and glycol.

The next step in Wislicenus' career should normally have been his "habilitation as Privatdocent" at the University of Halle, but his participation in liberal movements, both political and religious, barred the way, and he was informed that unless he left public politics entirely alone he would not be permitted to place his foot on this next rung of the academic ladder. Wislicenus was, however, not the man to be coerced by such methods, and, preferring freedom in a foreign country to bondage in his own, he migrated to Zürich, and became Privatdocent at the University there.

There is probably no city in Europe which has such a broadening influence on the human sympathies as Zürich; its atmosphere is unique. The intellectual centre of the Swiss Republic, it has become the asylum of many distinguished refugees and malcontents from the despotic states of the Continent, whilst its geographical position leads to its being traversed by a continuous stream of visitors of all nationalities throughout the year. In this international colony of free thought and uncompromising originality, and placed amidst the purest of democracies, there is no soil for the growth of those privileges attaching to birth and wealth with which so many other states are honeycombed. In Zürich you will not see "Liberté, Egalité, Fraternité," inscribed on the public buildings and posted up at the street-corners, but you will see these principles actually practised, and the man who is unwilling to conform to their spirit will find this city a very undesirable dwelling place.

The thirteen years (1859 to 1872) which Wislicenus spent amongst these surroundings were in many respects the most important of his life, and the experience he gained during this time must have largely contributed to the building up of that rare personality which always made him such a marked figure amongst his academic colleagues.

Wislicenus' career in Zürich was an extraordinarily rapid and brilliant one, more and more responsible posts in quick succession being entrusted to him by the Swiss Government. In 1861 he was made Professor of Chemistry and Mineralogy in the Cantonal School, in 1864 Extraordinary Professor, and in 1867 Ordinary Professor at the University, whilst in 1870 the still higher office of Professor at the Polytechnikum was conferred on him, and of this famous institution he became, in the following year, Director. It was in Zürich that Wislicenus carried out some of his most memorable researches, and began to display his great power of correlating isolated facts in support of wide generalisations. Thus in 1862 he published important papers referring to the constitution of the lactic acids, and supported his views by the experimental synthesis both of ethylene and ethylidene lactic acid. Then followed a long series of investigations on oxyacids, which had a most important influence on the development of structural organic chemistry, and ultimately led to a complete elucidation of the remarkable phenomena of isomerism exhibited by the lactic acids. Thus, when Wislicenus had proved that there were three isomeric lactic acids, whilst structural formulæ predicted only the existence of two, he did not hesitate to hazard the opinion before the "Naturforscher Versammlung" at Innsbruck in 1869, that this isomerism would be explicable by a consideration of the grouping of the atoms in space and by the use of solid model formulæ. In his own words—

"*Derlei feinere Isomerieen würden sich wohl durch räumliche Vorstellung über die Gruppirung der Atome, also durch Modellformeln deuten lassen.*" (Berichte d. deutschen chem. Gesellschaft, 1869, pp. 550 and 620.)

This pregnant suggestion was a few years later developed by Le Bel and Van't Hoff into an entirely new domain, now known as *Stereochemistry*, with most important and far-reaching consequences. This branch of chemistry has attracted an ever-increasing number of workers, by whose labours a vast amount of experimental material has been accumulated, the subject being one of surpassing interest, largely owing to its intimate connection with the chemistry of vital processes. To this field of enquiry Wislicenus himself again returned about twenty years later, and made some most important contributions both theoretical and practical, which are summarised in his classical memoir, "Ueber die räumliche Anordnung der Atome in organischen Molekulen und ihre Bestimmung in geometrisch-isomeren ungesattigten Verbindungen," published before the Königl. sächsische Gesellsch. der Wissenschaften in 1887. A most eloquent discourse on this subject was delivered by Wislicenus before Section B of the British Association in the same year, and formed one of the most memorable features of the Manchester Meeting.

During the Zürich period of his career, Wislicenus carried out, in conjunction with his friend Adolf Fick, then Professor of Physiology at the same University, what must be regarded as one of the most important and fundamental physiological experiments ever made, revolutionising as it did the doctrine introduced by Liebig, that albuminoids were the exclusive source of muscular power, and that the energy contained in the fats and carbo-hydrates was only employed in maintaining the temperature of the body. By climbing the Faulhorn (Bernese Oberland), on August 30, 1865, taking food only from which albuminoids were carefully excluded, and also determining the total nitrogen excreted during the climb, Fick and Wislicenus conclusively proved that the muscular energy was principally derived from the oxidation of fats and carbo-hydrates. In fact the energy liberated in the oxidation of albuminoids (as measured by excreted nitrogen) did not amount to one-third of that required to perform even that minimum of work involved in raising the body through the vertical height of the mountain. This classical experiment was shortly afterwards supplemented by the late Sir Edward Frankland's determinations of the heat of combustion of muscular fibre, and of numerous nitrogenous and non-nitrogenous food-stuffs, which threw quite new light on the total possible energetic values of these materials. (See Frankland's 'Experimental Researches,' London, 1877, pp. 918–959.)

Wislicenus having thus, by the fertility of his labours on foreign soil, won his way into the front rank of living chemists, it was not surprising that in 1872 he should have been called to Germany to occupy the Chair, rendered vacant in the University of Würzburg by the death of the celebrated Adolf Strecker. The filling of chairs by those who have distinguished themselves as university teachers in foreign lands has been of not unfrequent occurrence in Germany, and has proved a great source of academic strength to the country.

The thirteen years (1872 to 1885) which Wislicenus spent in Würzburg, were those during which his rare gifts were probably displayed to the greatest advantage. They were the thirty-seventh to the fiftieth years of his life. This period was principally occupied in a long series of investigations bearing on the constitution, reactions, and synthetic uses of that marvellous substance, *acetoacetic ester*, which had been independently discovered by Geuther, and by Frankland and Duppa some ten years previously. It would be difficult to say how many publications concerning this classical body emanated from the Würzburg laboratory during the Wislicenus *régime*, whilst still more difficult would it be to enumerate his pupils who were enabled to append the magic letters, "Ph.D.," to their names as the outcome of investigations which they had made on this fertile compound of carbon. These researches led not only to the elucidation of the constitution and reactions of acetoacetic ester itself, but to important further advances, such as the uses of malonic ester by Conrad, Bischoff, and Guthzeit, the synthesis of succinyl-succinic ester by F. Herrmann, the production of

polymethylene rings by W. H. Perkin, junior, and the synthetic formation of the pyridine ring by Hantzsch. All these achievements must be regarded as the direct result of the *Zeitgeist* prevailing in the laboratory, and of the inspiration derived from the master.

Of other investigations which emanated from the Würzburg laboratory during Wislicenus' tenure of office, mention may be made of the synthesis of hydantoic acid from cyanic acid and glycocoll, the synthesis of ethylmalonic acid by the action of potassium cyanide on the α-bromo derivative of normal butyric acid, researches on benzoïn, on biuret derivatives, on the constitution of phosphorous acid, on the production of guanidines by the interaction of mercuriphenylammonium chloride on thiocarbamides, and studies on the isomeric crotonic acids. During the later years also a number of his pupils were engaged in researches on the aromatic and camphor compounds. From this brief survey it will be sufficiently apparent that the investigations in his laboratory were spread over an unusually wide field of organic chemistry.*

Although during the Würzburg period Wislicenus was not actually engaged on any work relating to stereochemistry, the magnetic eloquence of his discourses on this fascinating domain doubtless led several of his Würzburg pupils—Hantzsch, Bischoff, Purdie, and others—to subsequently devote their best energies to extending its boundaries in various directions.

The remarkable strength of the University of Würzburg at this time, in the Faculties of Science and Medicine, may be gathered from the fact that Wislicenus numbered amongst his colleagues such men as Adolf Fick (physiology), v. Kölliker (anatomy), v. Bergmann (surgery), v. Gerhardt (medicine), Kohlrausch (physics), and Sachs (botany).

On the death of Kolbe, in 1885, Wislicenus was called to the Chair of Chemistry in the University of Leipzig, where the duty devolved on him of directing the energies of an even larger school of chemistry than at Würzburg. The demands made upon a professor of chemistry in one of the large universities of Germany can only be realised by those who have studied there, as they have no parallel in the present academic system of our own or any other country. The duties can only be properly performed by a man who combines commanding ability, extraordinary capacity for work, and iron physique.

This period of Wislicenus' career, which only closed with his death in 1902 (December 5), was distinguished by many researches of great importance, more especially those relating to the configuration of unsaturated organic molecules (fumaric and maleïc acids, the crotonic acids, angelic and tiglic acids, the stilbenes, etc.), and to the synthesis of cyclic compounds (reduction of diketones to cyclic pinacones).

In respect of its influence on the progress of organic chemistry, Wislicenus'

* For a complete list of Wislicenus' publications, see 'Berliner Berichte,' vol. 37 (1905), pp. 4928—4946, these eighteen pages being covered by the enumeration of their titles, joint authors' names, and references alone.

work falls into three parts, which are broadly coincident with his academic activity in Zürich, Würzburg, and Leipzig respectively. His work in each of these centres was destined to produce a far-reaching effect. The investigations on the lactic acids, carried out in Zürich, were, as already pointed out, largely responsible for the fertile speculations of Van't Hoff, and may thus be regarded as the foundation stones of structural stereochemistry. In his work at Würzburg on acetoacetic ester, the extraordinary value of this substance as a synthetic agent was displayed in a great variety of ways, and led not only to its extended use, but also indirectly to the discovery of numerous other agents of a similar character, and thus to a great multiplication of the methods available for building up carbon compounds. Lastly, by the speculative and experimental work in the domain of stereochemistry, which distinguished his tenure of the Chair at Leipzig, he provided the widest and most consistent explanation yet given of the phenomena of isomerism manifested by numerous unsaturated carbon compounds. It will be evident, therefore, that Wislicenus' influence is discernible far and wide in that extraordinarily rapid development of organic chemistry which took place in the latter half of the century that is just past.

That the great merit of Wislicenus' work was recognised by the world during his lifetime is attested by the public honours which poured in upon him. In this connection it will be sufficient to mention that he received high orders from the rulers of Bavaria, Saxony, and Norway, two of which carried with them the patent of nobility. It was, however, characteristic of the man that he consistently declined to make use of the titles which Courts had thrust upon him. He was elected a Foreign Member of the Chemical Society in 1888, and a Foreign Member of the Royal Society in 1897, receiving the Davy Medal in the following year.

Of much greater value to Wislicenus than the prizes of scientific societies and the favours of princes was the knowledge of the feelings of love and respect entertained for him by his pupils, and indeed by all who came into personal relations with him. Certainly it would be difficult to conceive of anyone more liberally endowed by nature with precisely those qualities which are calculated to win the hearts of men. The majestic form and classical features might have well served Phidias or Praxiteles as a model for the Olympian Zeus. His mellow voice and wonderful command of language, guided by artistic intuition and the purity of his spirit, led him to be acknowledged as one of the most magnetic and inspiring orators of Germany. His lofty idealism and unswerving devotion to duty he carried into every phase of life, and his aspirations he had the power of communicating to those with whom he came into contact. Without any touch of Puritanism in the ordinary sense of the word, for he was full of good-fellowship and the friend of conviviality, he was one of those men who purify all their surroundings. In Wislicenus' presence it was almost impossible for anyone to harbour a mean or unworthy thought, his searching though optimistic gaze irresistibly drawing forth the good and banishing the evil.

A man who thus combined such high qualities of heart and mind with a living enthusiasm for his science, could not fail to be a stimulating teacher. He gave the most conscientious attention to all students, from the beginner upwards, and sought in his daily visitation of the laboratories to awaken interest and sharpen the powers of observation and reasoning in his pupils, rejoicing with those that were successful in their investigations and encouraging to renewed effort those whom some failure had depressed. It was by means of this contagious enthusiasm and warm sympathy of the master that the great hives of industry at Würzburg and Leipzig were kept humming, and not by any visible disciplinary measures which are the resort of those who, although placed in authority, were never born to rule.

It was inevitable that one so full of human sympathy and with so much instinct for practical affairs as Wislicenus, should have been deeply interested in the momentous political changes through which Germany passed during his lifetime. The key to the political sentiments of his later life is to be found in the circumstance that he was at the still impressionable age of thirty-five in those stirring times when a united Germany was forged out of incoherent fragments by the determined men who brought to such a successful issue the great struggle of 1870. This united Germany, which had been the dream of the liberal idealists of the previous generation, was rendered an accomplished fact by a man, who, trusting in material strength alone, had no sympathy with liberal aspirations. Nevertheless, the great work actually accomplished by Bismarck and his iron associates in the drama of 1870, secured the unbounded admiration of Wislicenus, as it did also of so many other Germans who were both by nature and by tradition imbued with liberal principles. Such men felt that the ideal but abortive aspirations of 1848 must be sunk for the time at least, and that their immediate energies should be directed to the consolidation and expansion of the great empire which had been built upon the throne of the Hohenzollerns as a base. Thus in the latter half of his life we find Wislicenus an enthusiastic admirer of the Iron Chancellor, of the Emperor William, and of the military system; he was one of the founders of the "Alldeutscher Verband," and was amongst the first to urge upon his countrymen the necessity for increasing the strength of the German navy. In giving his unqualified support to these men and to these measures, it is evident that Wislicenus must have been drawn into that chauvinistic vortex which now for a generation has hung over the civilised world—like a great storm-cloud of ever-increasing density, but in which at length a small rift is beginning to appear in the shape of the newer idealism of those who dream not of empire but of the universal brotherhood of man. Could another decade have been added to the life and activity of Wislicenus, there can be little doubt that his powers of advocacy would have been enlisted in promoting that great work, which has already begun, of restricting the use, if not of limiting the power, of the sword on the earth.

Any account of Wislicenus would be wholly incomplete without a reference to his family life, the circumstances of which are responsible for the manifes-

tation of some of his greatest qualities. Soon after settling in Zürich, he married Katharine Sattler, who belonged to a Bavarian family remarkable for talent and originality, and who herself was possessed of great gifts as an artist. Her grandfather was with Russ, the inventor, in 1814, of the well-known pigment, *Schweinfurt-Green.* Wislicenus' domestic happiness was, however, destined to be of only short duration. In 1866 his brother Hugo, Privatdocent of German Archæology in Zürich, was killed in a mountaineering disaster on the Tödi, and a few years later his wife, to whom he was most devotedly attached, developed an incurable mental disorder, from which she suffered for upwards of thirty years. She died in 1904, and thus survived her husband by more than a year.

Wislicenus had four sons and two daughters, to all of whom he was attached with something more than fatherly affection, the bond of union being strengthened by the crushing sorrow resting upon the otherwise high-spirited and joyous children, over whom he watched with a mother's solicitude. Of the four sons, two were taken from him—Conrad in the first bloom of youth, and Alwin, who displayed extraordinary talent as a painter, under most painful circumstances in early manhood. Of the remaining two sons, the elder, Professor Wilhelm Wislicenus, was called to the Chair of Chemistry at Tübingen shortly before his father's death; whilst the younger, Professor Hans Wislicenus, had already some years previously been appointed to the Chair of Chemistry at the Agricultural Academy in Tharandt, Saxony. Of the daughters, the elder, Emilie, devoted herself absolutely to the father whom she loved so well, and for whose companionship she renounced, without murmur or hesitation, the artist's career for which she was so highly qualified. The second daughter, Marie, likewise endowed with artistic talents, married Dr. Adolf Fick, the well-known ophthalmologist, and it was her home in Zürich, as well as the homes of his two sons, which became for Wislicenus in his later years the holiday retreats in which the cares and sorrows of a lifetime could be forgotten for a few weeks amidst the radiant faces and the innocent prattle of grandchildren.

That Wislicenus' powerful physique was beginning to decline became apparent several years before his death, but he continued his lectures and attended to his other university duties until July, 1902. In the following vacation he sought relief at Wildbad from the rheumatic pains with which he had long been troubled, but the treatment did not lead to the beneficial results hoped for. He reluctantly yielded to the injunctions of his medical advisers and deputed his work for the whole of the ensuing winter session. The mischief had, however, already proceeded too far for remedy, and on December 5, 1902, he succumbed to a stroke of cerebral apoplexy in the sixty-eighth year of his life.

In Wislicenus the scientific world lost one of the most distinguished chemists of the 19th century, Germany a great orator and patriot, his friends and relatives a strong head and the warmest of hearts, ever ready with counsel or sympathy, and a pillar of strength in the hour of need or

tribulation. Lastly, his numerous pupils lament the loss of the master who not only fired them with enthusiasm for their science, but who also, by his great example of unswerving devotion to duty and of resolute fortitude in bearing adversity, inspired them to lead a higher and a nobler life.

P. F. F.

GEORGE JOHNSTON ALLMAN. 1824—1904.

GEORGE J. ALLMAN, born in Dublin on September 28, 1824, was a younger son of William Allman, M.D., who was Professor of Botany in the University of Dublin from 1809 to 1844. Dr. William Allman was one of the most distinguished botanists of his time, and was the first professor in the British Isles to introduce (in 1812), and lecture on, the Natural System of Linnæus.

George J. Allman entered Trinity College, Dublin, at an early age, and during his undergraduate course uniformly obtained high honours in Mathematics, pure and applied. He graduated in 1884 as a Senior Moderator and Gold Medalist in those subjects, along with the late Professor Samuel Haughton, F.R.S., who obtained the First Senior Moderatorship of that year. In 1853 he married Louisa, daughter of Mr. John S. Taylor, of Corballis, Co. Meath, and in the same year was appointed Professor of Mathematics in Queen's College, Galway; there he had among his colleagues Sir Thomas W. Moffett, late President of the College, George Johnstone Stoney, F.R.S., John E. Cairnes, the distinguished Political Economist, D'Arcy Thompson, and other men of celebrity. He was made a Member of the Senate of the Queen's University in 1877, and was nominated by the Crown, in 1880, one of the first Senators of the Royal University of Ireland, a position which he filled until the end of his life.

The degree of Doctor of Science (*honoris causâ*) was conferred on him in 1882, and he was elected F.R.S. in 1884. He was sent by the Council of his College as a delegate to the University of Bologna on the occasion of the celebration of its Octo-centenary in 1888.

The work by which Dr. Allman's name will long be known is his "History of Greek Geometry from Thales to Euclid," which first appeared in the form of successive articles in various numbers of the Trinity College periodical, entitled 'Hermathena,' and afterwards (in 1889) was published as a volume in the Dublin University Press Series.

To this work Dr. Allman devoted many years of indefatigable study, learned research, and original thought. In it he traced the rise and progress of the sciences of Geometry and Arithmetic, comprising the labours and discoveries of the three great schools of the period, known respectively as the Ionian, the Pythagorean, and the School of Athens. As remarked by Mr. J. S. Mackay at the end of a critical review in the 'Academy,' June 1, 1889, "Nothing so painstaking, so lucid, and so satisfactory has been written on the history of geometry during the period selected, even in laborious Germany." The work was hailed with high praise by scientific and literary journals at home and on the Continent; it was recognised, as having thrown a large amount of new light on the different steps in the early development of science, by distinguished foreigners, such as Tannery, of Paris; Zeuthen, of Copenhagen; Loria, of Genoa; Hultsch, of Dresden; Günther, of Munich; Cantor, of Leipzig, and other well-known mathematical scholars.

Dr. Allman had earlier published several mathematical memoirs, among which was an account of Professor McCullagh's lectures on the "Attraction of the Ellipsoid," which was reproduced in the collected works of McCullagh, published (1880) in the Dublin University Press Series. At a later period he contributed to the 9th Edition of the 'Encyclopædia Britannica' articles on Thales, Pythagoras, Ptolemy, and other Greek philosophers.

Dr. Allman died of pneumonia in Dublin, on May 9, 1904. In every relation of life he was estimable, and his loss will be long felt by a large circle of college and other deeply attached friends. To the latter he was endeared by his affectionate, frank, and genial disposition; and no person who came in close contact with him could fail to be impressed by the integrity, sincerity, and strong sense of duty which were among his marked characteristics.

B. W.

SIR ISAAC LOWTHIAN BELL. 1816—1904.

THE father of Sir Isaac Lowthian Bell, Mr. Thomas Bell, came to Newcastle in the year 1808. By birth he was a native of Cumberland, and he entered the offices of a Cumbrian firm, Messrs. Losh and Company. As it was in the employment of this firm that, some 30 years later, Sir Lowthian Bell was to take the first step of his business career, a few particulars of the work in which they were engaged may not be considered out of place.

Messrs. Losh and Company had carried on a general merchants' business in Newcastle, but at the time when Thomas Bell joined them they were launching out into other and wider directions. They had just started the Walker Alkali Works, using Le Blanc's process, and were, in addition, manufacturing malleable iron at Walker, obtaining the pig iron in Scotland.

A few years after his arrival in Newcastle, Thomas Bell married a Miss Catherine Lowthian, and in the year 1816 their son, Isaac Lowthian Bell, was born.

His early education may be said to have been very thorough. It began at that famous fount of learning, Dr. Bruce's Academy in Newcastle-on-Tyne. At that time most Newcastle youths of a certain standing seem to have attended Dr. Bruce's school. Many became very distinguished men, and though, in latter day Newcastle, their place knoweth them no more, yet the old school and its master are by no means forgotten. From this place young Bell passed first to Denmark and then to Germany; next to Edinburgh University, and finally to France. He studied in Paris for a time, and then went to Marseilles, where he learned a new process for the manufacture of alkali. On his return from France, being by this time 19 years old, he entered the offices of his father's firm, Messrs. Losh, Wilson, and Bell, in Newcastle. He only remained for about a year in Newcastle, and then was sent to Walker-on-Tyne to manage the firm's rolling mills there. His labours at Walker, and incidentally his connection with Messrs. Losh, Wilson, and Bell, seem to have lasted for about the next eight or ten years. This period may be said to have completed his education, if such an expression be permitted of one who continued to acquire knowledge during the whole of his life. Certainly during this time he was taught, and taught himself, a great deal.

He had the advantage of considerable intercourse with Lord Dundonald in connection with the manufacture of railway wheels, which the firm were making under the latter's patent. Lord Dundonald, so well known to history in other spheres of distinction, was not only a man of alert intellect, but also one of considerable scientific attainments. Probably of all Lowthian Bell's instructors, a Mr. John Vaughan, with whom he first came into contact about

the year 1842, was the one to whom he owed most. Mr. Vaughan must have been a very remarkable character. He came from Carlisle to look after the rolling mills at Walker. He was, of course, a professor of rule of thumb, but at the same time one imagines that he knew in his own way practically all that was then known about iron. It is an interesting picture, which we have from the pupil's own lips, of these two at their work. They would sit in the mill and watch the work going on, most of the day and often half the night, the elder man expounding, and the youth absorbing, information, which later on he was to translate into the language of science.

In the meantime Mr. Bell had married Miss Margaret Pattinson, and had removed from Newcastle to a house at Benton. His father-in-law, Mr. Hugh Lee Pattinson, was a Fellow of the Royal Society, and was interested in the Felling Chemical Works. It seems to have been at about this time, or a year or two later, that Mr. Bell severed his connection with Messrs. Losh, Wilson, and Bell.

In the year 1844, with two of his brothers, Thomas and John Bell, he took a lease of Captain Blackett's blast furnaces at Wylam-on-Tyne, a venture which, as it turned out, had the most far-reaching results. It was this combination which, in a few years' time, was to become famous as Messrs. Bell Bros.

Their business started upon a moderate scale. Their iron ore was obtained at first from Hareshaw in Northumberland, and afterwards ironstone was collected on the beach at Whitby. Subsequently they used material from the mines at Skinnergrove in Yorkshire.

There is a curious story in connection with this phase of the firm's existence. It was while the Messrs. Bell were working the mines at Skinnergrove that Mr. Bewick, the geologist, told them that he knew where an ironstone bed, 10 feet thick, existed. He refused to disclose its exact locality, as he said that it was far from any railway, and would ruin them if they tried to work it. As a matter of fact, it was at Skelton in Yorkshire, and subsequently Messrs. Bell Bros. became lessees of it.

About the year 1850 Mr. Lowthian Bell assisted his father-in-law to start the Washington Chemical Works. He was connected with this concern for a number of years; in fact, for nearly twenty he lived at Washington, but in spite of this it does not appear that he took quite the same interest in the Washington business as he did in that of Bell Bros.

He eventually, in 1874, parted with his shares in the Washington Company to his two brothers-in-law, Mr. Newall and Mr. Beaumont.

In so many ways, from about the year 1850, is Mr. Lowthian Bell's history the history of Bell Bros., that it would perhaps be easier to trace—at first at all events—the progress of the firm rather than that of the individual.

At this time, then, the great Cleveland ironstone bed had just been discovered, and, in the year 1852, Messrs. Bell Bros. became lessees of a portion of it on the Normanby estate, which was the property of the Ward-Jackson family. After they had obtained, with no little difficulty, this lease, Bell

Bros. determined to open furnaces in closer proximity to their supply of ironstone. This necessitated a great deal of negotiation and a great deal of arrangement, but ultimately the Clarence Works were started on the north bank of the Tees, at what was afterwards to become the town of Middlesbrough. The exact reason for the choice of this spot is believed to have been on Mr. Ralph Ward-Jackson's account, who was one of the owners of the Normanby estate. Further difficulties arose in connection with the railway transport of the ironstone, but eventually the firm obtained an Act of Parliament for the construction of the Cleveland Railway. This result, however, was not reached without severe fighting, for even after the Parliamentary conflicts, which in themselves were memorable, the opposition was not at an end; but the railway was completed at last, and the ironstone was thus brought direct to the furnaces.

In 1854, three furnaces at the Clarence Works were put into blast. There were only two rival establishments on the Tees at this time, Messrs. Bolckow, Vaughan and Company and Messrs. Cochrane and Company.

For the first few years the company seem to have done extremely well. Prices for pig iron were high, and the business was very ably managed.

In 1858, owing to the growth of the Clarence Works, the Normanby supply of ironstone was found to be insufficient, and in consequence of this the firm obtained a lease of a larger tract of country on the Skelton Castle estate. This, it will be remembered, was the El Dorado mentioned by Mr. Bewick.

But lean years were to follow, and in 1861 we hear of pig iron at 44*s.* instead of 71*s.*, as in 1854. However, Messrs. Bell Bros. managed to carry on their works, owing to the careful manner in which their business had been conducted during the prosperous times.

It was at about this time that the West Hartlepool Harbour and Railway Company, who were deeply interested in several collieries in the county of Durham, found themselves, owing to the general depression in trade, unable to carry on their business. The actual railway and harbour works were sold to the North-Eastern Railway Company, of which Mr. Lowthian Bell was made a director in 1865, and Messrs. Bell Bros. were able to purchase a portion of their colliery property.

Thus, in 1864, they became proprietors of the Page Bank Colliery, and in the same year they sank the Brownie Colliery on a large tract of coal which they leased from the late Lord Boyne.

This does not, by any means, exhaust the list of their colliery properties, but will suffice to show that Messrs. Bell Bros. were expanding very rapidly. And in each step of their progress one traces the careful guiding hand of Mr. Lowthian Bell, for it is impossible not to be impressed by the shrewdness and prudence of the policy of the firm. In fact, throughout Mr. Bell's life, one notices the same far-sightedness in connection with almost everything with which he had to do.

In 1874 the firm of Bell Bros. became a limited liability company, and of

its history from this point onward a few words will suffice for the purpose of this memoir. Mr. Lowthian Bell did not in any way lose interest in his works; indeed, so far from this being the case, in the course of the next 20 years he acquired practically the whole of the shares in the company. However, the subsequent development of Bell Bros. is better known than its earlier history, and any worthy account of it would occupy too much space to be here introduced. A word may be permitted, however, with regard to the Clarence Works of the present day. They represent, under favourable conditions of trade, an output of about 1000 tons of iron a day. Their rolling appliances are capable of dealing with some 1500 tons of steel ingots, and the number of men employed is about 5000. *Exegit monumentum* might well be said.

Having dealt, though not by any means fully, with Sir Lowthian Bell's commercial career, his scientific achievements may now be considered.

From almost his earliest years he had a considerable leaning towards chemistry. As we have seen, he devoted much of his time to the scientific side of alkali making. And there can be little doubt that, but for his subsequent researches on iron, which rendered him so famous, and which fully occupied him, his work on this subject would have earned for him the highest consideration as a practical chemist.

But, as has been stated, it was in connection with the metallurgy of iron that his chief work was accomplished. For the last 50 years of his life he had few superiors in general knowledge of the subject, and as far as the blast furnace is concerned he was probably without equal. He it was who first endeavoured to explain the actual conditions which exist inside a blast furnace, and to his investigations was due, to no small extent, the discovery of the Thomas-Gilchrist process.

In 1872 he published that standard work of reference, for all who are interested in the manufacture of pig-iron:—

"Chemical Phenomena of Iron Smelting: An experimental and practical examination of the circumstances which determine the capacity of the blast furnace, the temperature of the air and the proper condition of the materials to be operated upon."

Twelve years later he published a second work, "Principles of the Manufacture of Iron and Steel."

These two books made his name as a metallurgist in scientific circles, and it is not surprising that numerous honours from the learned societies of England and America fell to his share. Among others may be mentioned the Gold Medal of the Society of Arts and the Bessemer Gold Medal of the Iron and Steel Institute. Of the latter body he was ever a warm supporter. He was instrumental in its foundation, and in 1873 succeeded Sir Henry Bessemer as its third President. He was an Hon. D.C.L. of Durham University, LL.D. of Edinburgh and Dublin, and D.Sc. of Leeds University.

Of his municipal and political work, little need be said. He was for many years a Councillor, and then an Alderman, of Newcastle-on-Tyne, and was

Mayor of the city on two occasions, one of his terms of office being for 1863, when the British Association visited Newcastle, Lord Armstrong being President. As a Liberal he sat in Parliament for a short time, representing the Borough of Hartlepool, and previous to this he had unsuccessfully contested the Northern Division of the County of Durham.

Apart from his own business he devoted much of his time, especially towards the end of his life, to the affairs of the North-Eastern Railway Company. Only a short time before his death he published an exceedingly useful volume, the result of his investigations on the life of a steel rail.

He served on more than one Royal Commission, and was a Government Commissioner or Juror for most of the International Exhibitions for the last thirty years. In the year 1885, to mark his services to the State, he received the honour of a baronetcy.

Little remains to be said: his latter years were spent at Rounton Grange in Yorkshire, a place which he purchased early in the seventies. Time seems to have dealt very gently with him, and though he reached a great age, his faculties, with the exception of his eyesight, were almost unimpaired. During the last year of his life he failed somewhat, and finally on December 20, 1904, in his eighty-ninth year, he passed away full of years and of honour.

A. N.

FRANK McCLEAN, 1837—1904.

FRANK McCLEAN, who died at Brussels on November 8, 1904, was born at Belfast on November 13, 1837. He was the only son, in a family of six, of John Robinson McClean. Mr. McClean, senior, was a civil engineer and Fellow of the Royal Society. His eminence in his profession and his reputation as a man of sound judgment are indicated by the fact that he was a member of several Royal Commissions. His advice was also sought by the Emperor Louis Napoleon about improvements in the City of Paris, and he was one of the English engineers who urged the completion of the Suez Canal at a time when the abandonment of that great work was contemplated by the Khedive.

Frank McClean was educated at Westminster School up to the age of sixteen, and went thence to Glasgow University, where he came under the influence of Sir William Thomson, now Lord Kelvin. In 1855 he entered at Trinity College, Cambridge; he became a scholar of the College and was a Wrangler in the Mathematical Tripos of 1859. Immediately after taking his degree he became a pupil of Sir John Hawkshaw and was employed on the drainage works of the Fen Districts of the Eastern Counties. In 1862 he was made a partner in the firm of McClean and Stileman and assisted his father in the survey made for the railways in Moldavia. Shortly afterwards he became resident engineer of the Barrow Docks and of the Furness and Midland Railway and acted in this capacity for about four years. In 1865 he married Ellen, the daughter of Mr. John Greg, of Escowbeck, Lancaster, and for the next four or five years lived in London, working in the office of the firm; but in 1870 he withdrew from the active pursuit of his profession and went to live at Ferncliffe, Tunbridge Wells.

Here he found quiet and leisure for congenial studies and for scientific research, and he devoted himself quietly and methodically to work. As an example of his thoroughness, it may be mentioned that on finding his studies seriously impeded by his ignorance of foreign languages, he mastered both French and Italian in his thirty-fifth year, and he read widely in ancient and modern history. He travelled much on the Continent and knew the principal galleries and museums intimately. His own superb collections of ancient coins, manuscripts, early printed books, enamels and ivories were made methodically; he did not collect in a haphazard way, he had an ordered plan, and as far as he could he chose his specimens to illustrate evolution in art. He did not often talk of these matters, but now and then he would open out and let one see the value he attached to the humanizing influence of art, his delight in some finished piece of workmanship and his knowledge of its position and value in the history of artistic

development. He thought that scientific men were often too much absorbed in their own special work. Perhaps he felt that his own method of research left him somewhat isolated; for he never employed an assistant, but carried out all the laborious details of his scientific work with his own hands; thus, for instance, in his very brief account of his study of the spectrum of high and low sun, he gives details of the methods he himself employed for the sensitisation of the photographic plates. So, also, his many portfolios of photographic enlargements which he himself made from his original negatives of spectra show how systematically he carried out the tedious processes of manipulation for the sake of being able to put into the hands of other investigators the material which he had gathered together by his own industry. The same sort of activity and system are evidenced by the choice collections which he bequeathed to the University of Cambridge for preservation in the Fitz-William Museum. The manuscripts which he bequeathed are 200 in number and range in date from the eighth to the eighteenth century; and there are besides 230 early printed books. By his bequests the resources of the Museum have been nearly doubled in each of these departments.

Mr. McClean's earliest scientific paper is a note of two pages on the Equations of the Motion of the Moon, published in the 'Quarterly Journal of Mathematics' in 1860; but he did not pursue this line of research, and it is in connection with spectroscopy that he made his mark in science. His first experimental work related to electricity; in 1872 he spent much time in devising and making coils and other electrical appliances, and he made use of them later in his researches on the spectra of metals. Meanwhile, about 1875, he invented the simple and efficient star spectroscope which bears his name. He used it in connection with a 15-inch reflector in making visual observations of star spectra at Ferncliffe. This form of spectroscope is a direct-vision instrument; it is furnished with a slit, which, however, may be dispensed with in stellar observations; in place of the usual plano-convex lens a cylindrical lens is inserted between the slit and the prism, and thus a lengthened image of the slit is formed in its principal focal plane. The observer thus sees a broad spectrum in which the lines can be much more readily detected than in the linear spectrum of a star. Mr. McClean has not given any published account of this instrument, but he had it constructed by Browning; and by reason of its compactness and efficiency, and the ease with which it could be manipulated, it was and still is widely used.

Mr. McClean's first published paper on spectroscopic matters is one relating to his photographs of the red end of the solar spectrum between the lines D and A ('Monthly Notices, Royal Astronomical Society,' 1889, vol. 49, 122–124). He had been for several years previously working at solar observations, and for three years at least, 1879–81, had made records of the positions and drawings of the forms of the notable prominences on the sun's limb. These records survive unpublished, but it is only from a question put to Father Perry at a meeting of the Royal Astronomical

Society in January, 1888, that we learn that he had paid attention to solar phenomena for nine years previously. He remarked at that same meeting that his observations afforded some evidence of the recurrence of prominences at fixed solar longitudes, and that there seemed to be indications that prominences were of a more permanent character than sun-spots. The records, which are fairly numerous for 1879–81, seem hardly to be sufficient to establish this view; the systematic nature of the observations was no doubt interrupted by his building a new house at Rusthall, Tunbridge Wells, whither he moved in 1884. He had arranged the spacious attics of the house, so as to serve as a laboratory, with electrical and other appliances. In the roof was fixed a polar heliostat which reflected sunlight down a telescope which pointed to the pole. By a second reflection the light passed into a diffraction grating spectroscope. This installation was designed for solar studies and for researches on the spectra of the metals. At the west end of the house he erected an observatory containing an equatorial of 8 inches aperture.

It was in 1887, very shortly after the completion of his new house and laboratory, that Rowland's map of the solar spectrum first appeared; this map exhibited the spectrum from wave-length 3200 to 5790. Now Mr. McClean had worked much in the red region of the spectrum, and this part was not delineated in Rowland's first map. In fact, nearly one-half of the visible spectrum remained to be photographed. Mr. McClean devoted himself to carrying out this work, and gave a brief description, in the paper of 1889 referred to above, of the photographic methods adopted, and issued a portfolio of enlargements of the solar spectrum from D to A in seven sections corresponding to those of Ångström's normal solar spectrum. This work was completed in December, 1888, almost simultaneously with the publication of the final edition of Rowland's map, which covers the range 3100–6950. Mr. McClean's work was done with a Rutherford grating from 1879 until 1890. In 1890 he substituted a Rowland plane grating.

Mr. McClean next embarked upon a more extensive piece of work, part of which he carried out and published in the form of a portfolio of "Comparative Photographic Spectra of the Sun and the Metals." Series I relates to the platinum group of metals, and shows the solar spectrum and the spectra of iron, platinum, iridium, osmium, palladium, rhodium, ruthenium, gold, and silver. The range of spectrum shown is from 3800 to 5750; it is divided into six sections corresponding to the sections of Ångström's chart, the scale of the plates being 1 mm. per tenth-metre throughout. Series II deals in similar manner with the metals of the iron-copper group, viz., iron, manganese, cobalt, nickel, chromium, aluminium, and copper. He had begun the work by taking comparative photographs of the sun, iron, and iridium; iridium was chosen in order to get a full spark spectrum of air; iron was chosen "on account of its close correspondence with the solar spectrum, and its thus furnishing the best means of co-ordinating the spectra of the other metals with the solar spectrum."

In November, 1890, Mr. McClean had completed his "Comparative Photographs of High Sun and Low Sun Spectra," showing the absorption lines due to the earth's atmosphere. This paper is the last which he published dealing with solar phenomena.

In 1895, Mr. McClean set up in the observatory on the roof of Rusthall House a fine twin refractor made by Sir Howard Grubb. It was of the pattern used for the astrographic chart and consisted of a 10-inch visual telescope coupled with a 12-inch photographic; it carried also an objective prism of 12 inches clear aperature with an angle of 20°. It was thus in his fifty-ninth year that Mr. McClean embarked with this instrument on a systematic survey of the spectra of the stars brighter than $3\frac{1}{2}$ magnitude in the northern heavens. This survey was completed in 1896, and the general results, together with 17 plates reproducing the spectra of 160 stars, were published in the 'Transactions' of the Royal Society in May, 1898. Meanwhile Mr. McClean had completed the survey of the whole sky by taking his objective prism to the Cape of Good Hope, where Sir David Gill put the astrographic telescope of the Royal Observatory at his disposal. With this he had in six months secured 292 photographs of the spectra of 116 stars. In the Northern Survey one of the results of interest was that the bright helium stars were more numerous, relatively to other stars, near the galactic plane than near its poles. This point was amply corroborated by the Southern Survey. A further result of interest in the latter survey was the discovery of the fact that oxygen is shown by the visibility of several characteristic lines in the spectrum to be present in many of the helium stars.

The Gold Medal of the Royal Astronomical Society was awarded to Mr. McClean in 1899 for the achievement of this remarkable piece of work.

Among his other work may be noticed his researches on the spectrum of the variable star β Lyræ, published in 1896, and his work on Nova Persei, carried out in his sixty-fifth year, and published in 1905, after his death.

Of the inner history of the many munificent gifts and bequests which Mr. McClean made for the advancement of science, it is not easy to speak, for he was reticent about such matters. He showed his affection for his Alma Mater Cambridge by several endowments. First of all, in 1890, he founded the Isaac Newton Studentships; and it was characteristic of him that he declined to allow his own name to be attached to these endowments. The Isaac Newton Studentships were intended to encourage post-graduate study and research in astronomy (especially gravitational, but including other branches of astronomy and astrophysics) and physical optics. The studentships afford opportunities for men to devote themselves for three years to research at a time in their lives when, under ordinary circumstances, it would be necessary to search for other paid employment. The records of the holders of the studentships afford a remarkable testimony to the success of the endowment.

Again, it was Mr. McClean who, as an anonymous donor, gave a consider-

able sum in 1903 for the augmentation of the stipends of two distinguished mathematical lecturers at Cambridge. By this endowment the Stokes and Cayley lectureships were founded.

In 1894 Mr. McClean proposed to Sir David Gill to provide a large photographic telescope fitted with very complete spectroscopic appliances for the Royal Observatory at the Cape of Good Hope, in order that the attack on celestial problems might be carried on with greater power in the Southern Hemisphere. This equatorial, with large circumpolar motion, is a twin refractor, by Grubb, consisting of an 18-inch visual telescope coupled with a 24-inch photographic telescope. The design embodies suggestions made by Mr. McClean himself. An excellent dome fitted with hydraulic appliances for raising the floor was also provided. At Mr. McClean's desire, the telescope was called the Victoria telescope; he was in hopes that it would be completed in the year of the Diamond Jubilee of the late Queen; but sundry alterations were found necessary in the instrument, and it was only formally installed a couple of years later. He had intended to accompany the British Association to South Africa in 1905, principally with the object of seeing his telescope in use. Unfortunately this intention was frustrated, for he was overtaken by illness at Brussels on his way home from abroad; pneumonia unexpectedly developed, and he died at Brussels on November 8, 1904, in the 67th year of his age.

It was not merely during his lifetime that he was a generous benefactor of science. On his death it was found that he had left large bequests to be devoted to the improvement of the astrophysical equipment of the Cambridge Observatory: to the University of Birmingham (in which he had already shown his interest by liberal subscriptions during his lifetime) for the department of physical science: to the Royal Society: to the Royal Astronomical Society: and to the Royal Institution.

Mr. McClean received the honorary degree of LL.D. from the University of Glasgow in 1894. He was elected a Fellow of the Royal Society in 1895, and was for many years a Fellow of the Royal Astronomical Society, and a member of the Institute of Civil Engineers.

H. F. N.

ALEXANDER WILLIAM WILLIAMSON, 1824–1904.

AMONG the chemists engaged, in the middle of the nineteenth century, in developing the molecular theory of chemical reactions, it was Alexander William Williamson who established that theory on a foundation of experimental facts. His earlier researches on bleaching salts and on Prussian blue are of exceptional value and interest, but it is for the effect upon chemical theory of his other researches and essays that Williamson's name will remain eminent in the annals of chemistry.

Williamson did all his memorable work well within the first half of his life, indeed almost within the first third. His communications to learned societies concerning this work occupy so small a volume, notwithstanding their great significance, that an analysis of their contents can fortunately be included in this account of his life, without altogether exceeding the limits within which it must be confined. Usually, in preparing a biographical notice, famous investigations may be taken to be well enough known to make mention of them all that is necessary, but of Williamson's work a more particular account than that seems called for. There is, it would seem, at the present time, an insufficient realisation of what exactly Williamson did for chemistry, attributable, no doubt, to the fact that his efforts were directed to the replacement of notions, now almost obsolete, by those which have become part of the accepted theory of chemistry, as well as to the fact that the substances upon which he worked are among those which are best or most familiarly known, namely, bleaching powder, Prussian blue, and alcohol.

Of Scottish descent, Williamson was born at Wandsworth, in London, on May-Day, 1824. His father, a man of unusual force of character, was a clerk in the India House, but must have retired, with pension and private means, some fifteen years after the birth of his son. Williamson's mother was the daughter of William McAndrew, a city merchant; from her training and example he acquired that delicate sense of honour for which he was noted. When Williamson was six years old, the family removed from Camberwell to a house which his father had purchased in Wright's Lane, Kensington. James Mill and his son, John Stuart Mill, lived close by, and the two families formed an intimacy which was maintained for years afterwards. The old residences and gardens in Wright's Lane have long since been destroyed and their sites built over. At a date unknown, but probably coincident with that of his father's retirement from the East India Company's service, the family went abroad and resided for many years, first in Paris and then near Dijon. He attended day schools in Kensington, and apparently in Paris, and was a pupil at the College at Dijon. At Dijon also he and his sister, Antonia Helen, two years his senior, had private lessons. Concerning these, the tutor's report was that the young lady had worked steadily, but that of her

ALEXANDER WILLIAM WILLIAMSON.

brother as much could not be said.* Later on, Williamson spent a winter at Wiesbaden, working diligently at German. He spent three years (1841–4) at Heidelberg, where he went to study medicine at the wish of his father. He attended Tiedemann's lectures there; but the professor was then very old, and Williamson, finding the lectures intensely dull, spent much of the hour in conversation with Moleschott (to be well known later as a physiological chemist) and other fellow-students. On the other hand, he became greatly interested in his work in Gmelin's laboratory and with the lectures on chemistry. From the very first Gmelin was most kind and courteous, and later on he took the greatest interest in his successes. Williamson always spoke of Gmelin with the greatest respect and affection, and soon informed his father that he wished to be a chemist. The latter showed much annoyance, but, seeing that his son was determined, he wrote home to a relative to ask him whether there was any opening for a chemist in England. It will excite no surprise to hear that the answer returned was—"None at all." Williamson was also discouraged at first by Gmelin himself, who told him that it was not likely that he could succeed as a chemist, because of certain bodily imperfections. From earliest infancy he had lost much of the use of the left arm through stiffness of the elbow; and he had also been deprived of sight in one eye, and left very short-sighted in the other. It was not long before Gmelin had changed his opinion, and therefore allowed himself to tell Williamson's mother that her son "would be chemist." The mother being won over to her son's wishes, the father at length gave way.

Williamson next went to Giessen to study under Liebig. In six weeks' time (May, 1844) he was working daily in Liebig's laboratory, and rising early each day to attend Bischof's lectures on physiology, then his favourite science next to chemistry. During his stay in Giessen he boarded with the family of Dr. Hillebrand, Professor of Literature in the University. His associates were always his seniors, and his letters to his father at this time exhibit him as the serious and hard-working student, to whom even his recreations counted more as aids to better working than as enjoyments. It must be remembered that he had had no English school or college life worth considering, and that he was not bodily fitted to join in youthful sports.

Referring to Liebig in one of his letters, Williamson expresses the opinion that the eminence which that chemist had then reached, was due as much to his pleasing manner as to the undoubtedly great importance of his discoveries. There was to be added to this, he continues, that everyone coming in immediate contact with him could not but be captivated by the expression of benevolence or of affection which a look of his could convey.

Thirty years afterwards, in his Presidential Address at Bradford to the

* In the obituary notice of Williamson in the 'Journal of the Chemical Society,' Professor Carey Foster gives an interesting reminiscence of the striking personality of Antonia Williamson, to whom her brother through life showed the warmest attachment.

British Association, soon after the death of Liebig, he said of him and of these days in his laboratory, "I think it is not too much to say that the Giessen laboratory, as it existed some thirty years ago, was the most efficient organisation for the promotion of chemistry which had ever existed. Picture to yourselves a little community, of which each member was fired with enthusiasm for learning by the genius of the great master, and of which the best energies were concentrated on the one object of experimental investigation."

First Paper: Bleaching Salts, Catalytic Action.—While at Giessen, Williamson, at the age of 20, published in London, in the *Memoirs of the Chemical Society* (1844), the results of his first research. More as an exercise than for purposes of investigation, Liebig set him to work upon the subject of the "bleaching salts" which had recently been receiving attention in France, and even in Germany in the Giessen laboratory itself. He soon obtained results quantitatively at variance with those recorded by others, and came upon a fact which, in his own words in a letter to his father, "will throw a much-needed light upon the composition and properties of one of the most interesting salts, not only to the chemist but to the public." To Williamson's mortification, Liebig at first discredited these results as too improbable, but he was eventually convinced, exclaiming, to his pupil's delight, "Ei, das ist ja charmant, das ist allerliebst; jetzt bin ich erst überzeugt."

It may be of interest to record some words of Williamson's concerning the execution of this research. Writing of his solitary walks on Saturday afternoons, he says: "I often find such a walk of as much real service to me in my progress as a whole week's labour (in the laboratory). The great difficulty in a research such as that I am now pursuing consists not so much in performing the experiments once fixed upon, as in inventing and choosing from those most calculated to attain the desired object."

The great value of this paper, which is entitled "Decomposition of Oxides and Salts by Chlorine," as a contribution to the knowledge of the way in which bleaching salts in solution pass into chlorate, seems to have been entirely overlooked. Yet no one, after Balard and Gay-Lussac, has thrown more light upon the chemistry of chlorine in interaction with bases than Williamson.

As ordinarily carried out, the production of a chlorate is the result of the catalytic action of chlorine upon the hypochlorite present in the solution of (so-called) chloride of lime or similar bleaching salt; this Gay-Lussac had already explained. But Williamson succeeded in showing, in the first place, that, after the chlorine in presence of water has combined with an alkaline earth or an alkali to form chloride and hypochlorite of the metal, still as much more of it can be made to dissolve in the solution by converting the hypochlorite itself into chloride, along with hypochlorous acid, and with but very little formation of chlorate. In the next place, he found that this solution of metallic chloride and free hypochlorous acid can be made by heat to pass into that of chlorate equivalent in quantity to half of the

chloride, with the liberation of as much chlorine as had been absorbed by the bleaching solution. To make his proof of this the more convincing, he dissolved some potassium chloride in a strong solution of hypochlorous acid, and by heat changed this chloride into chlorate and free chlorine, thus establishing what had seemed to Gay-Lussac (1842) to be most unlikely. To-day, the possibility of such a remarkable change will be admitted without much hesitation; but 60 years ago, quite possibly, chemists hesitated to accept results obtained by a 'prentice hand in chemistry which were not in accordance with the opinion of such an authority as Gay-Lussac. Nearly 40 years later (1883), Lunge and Naef, evidently unaware of what Williamson had done, succeeded in showing that, even in the cold, hypochlorous anhydride freely decomposes solid hydrated calcium chloride by converting part of it into hypochlorite.

Finally, Williamson proved (contrary to what Liebig had with approval allowed his English pupil, Detmer, to publish in the *Annalen*) that hypochlorous acid, which so readily decomposes a chloride, cannot decompose a dissolved alkali carbonate or bicarbonate. By this, as he pointed out, it is shown that, in the copious production of a chlorate which may follow upon the passage of chlorine gas through a solution of potassium or sodium bicarbonate, the production of the chlorate depends solely upon the interaction of the first-formed alkali chloride and hypochlorous acid.

This research of Williamson's appears to be the first successful attempt to throw light upon the nature of a catalytic action, such as had been here presented by Gay-Lussac. It was soon to be followed by a second one in the case of what is known as etherification.

Ozone.—A second paper quickly followed that on chlorine. It is entitled, "Some Experiments on Ozone,"* and purports to have proved that ozone is a peroxide of hydrogen. Ten years afterwards, however, Andrews and Tait proved that ozone is not a compound at all. Williamson had worked with a mixture of ozone and oxygen electrolytically obtained, and these mixed gases, we must assume, had not been kept quite free from electrolytic hydrogen.

Prussian Blue.—Very soon after the appearance of the paper on ozone, Williamson published his important research on the composition of Prussian blue. This beautiful preparation was then of special interest as a salt, in the constitution of which one and the same element, iron, functions partly as basic and partly as acid radical. It had been easy to ascertain that it is composed of both ferrous and ferric cyanides and of potassium cyanide, and that the proportions of these cyanides are inconstant in it. It had also been possible to foresee, with some confidence, that among its component substances, there must be present the two cyanides of iron, formulated respectively by $Fe_7C_{18}N_{18}$ and $Fe_5C_{12}N_{12}$, but it had hitherto not been possible to verify this inference. For, Prussian blue, being amorphous and highly colloidal, is incapable of being separated into the several substances of which it is a mixture.

* 'Mem. Chem. Soc.,' 1845, vol. 2, p. 395.

Williamson succeeded in actually preparing both the above indicated iron cyanides in a state remarkably near to purity, notwithstanding their colloidal nature. He also produced a new blue salt, a constituent likewise of Prussian blue, a double cyanide of iron and potassium, $KFe_2C_6N_6$, by the limited oxidation of the insoluble, nearly white, potassium ferrous cyanide $K_2Fe_2C_6N_6$, known as Everitt's salt. The new salt, since obtained in various ways, has proved to be of perhaps greater interest than either of the other constituents of Prussian blue, namely, Turnbull's blue, $Fe_5C_{12}N_{12}$, and the substance, $Fe_7C_{18}N_{18}$, which chemists often still call "Williamson's blue." One thing which gives it interest is the fact that it is the parent salt of both Turnbull's and Williamson's blues, being always, as Skraup has shown (1875),* the precipitate first to form, whether a ferrocyanide be mixed with a ferric salt or a ferricyanide with a ferrous salt, so that, as a consequence, well-washed and freshly prepared Prussian blue is always a mixture of these three blue salts and of these only. Another point of interest about Williamson's new salt is the remarkable readiness with which it usually passes into a form freely soluble in water. It appears to be possible, indeed, to get all three blue constituents of ordinary Prussian blue into solution in water, but such dissolution of two of them only exceptionally occurs; whereas the other one, that obtained by Williamson, $KFe_2C_6N_6$, is usually found to be so soluble in water as to have become known as "soluble" Prussian blue, and is only obtainable in a form insoluble in pure water when it is prepared by Williamson's method.

One other matter of importance comes out from Williamson's researches on this subject, which is that, when potassium ferrocyanide in solution is digested with Prussian blue, the ferric cyanide in each of the three blue salts which together constitute it, will always take potassium cyanide from the ferrocyanide and thus become potassium ferricyanide in solution, whilst in its place there will be left an insoluble pale blue substance containing all the ferrous cyanide together with some of the potassium cyanide of the potassium ferrocyanide, apparently as Everitt's salt. Williamson proposed in this way to manufacture potassium ferricyanide in a state of purity.

From the account just given it will be seen that this paper on the compounds of cyanogen and iron must be ranked as a classic memoir on the subject. It was read at the meeting of the Chemical Society, held on March 16, 1846.

After carrying out the three researches just described, Williamson left Giessen and took up residence in Paris in July, 1846, where he remained until his return at last to London in June, 1849. Arrived in Paris, and being already familiar with the French language, he at once arranged for lessons in mathematics with Auguste Comte. Writing to his father in eulogy of Comte, he said, "If my experience of Comte's superior powers were insufficient to convince you that his lessons were worth their price, John (Stuart) Mill's

* Recent valuable work by Karl Hofmann and his colleagues on Prussian blue (1904–5) is essentially confirmatory of that of Williamson and of Skraup.

saying that he 'would prefer him to any man in Europe to finish a scientific education,' ought to carry the point and to induce you to consent to my continuing as I have begun." Williamson seems to have made good use of these lessons, for before the end of the year he was himself teaching an English youth mathematics. Comte was much pleased at this, and remarked that teaching was the best possible means to perfect one's own knowledge.

During Williamson's three years in France he published nothing of importance and seems not to have attempted any chemical researches. But it was probably in these years that he began that cordial acquaintance with Laurent, Gerhardt, Dumas, and other French chemists which continued throughout their lives. After his marriage, there was a close intimacy between the Williamson and the Wurtz families and also with the Berthelots, and with Cornu.

On the death of Fownes, Williamson, in 1849, was unanimously elected to the Professorship of Practical Chemistry in University College, London, and thus came under the influence of Thomas Graham, who at that period held the Chair of General Chemistry.

During the next five years he elaborated the great work of his lifetime publishing the results of it in varying detail at meetings of the British Association, the Chemical Society, and the Royal Society, and in the 'Philosophical Magazine' and the 'Chemical Gazette.' Of these researches, first came those included under etherification, and later those on the constitution of salts.

Etherification (1850-52).—The expectation that in chemical reactions substances would generally beget others similar to themselves, induced Williamson to make an experiment, soon to become celebrated, in which it was anticipated that a new alcohol could be derived from ordinary alcohol. To his "astonishment," it yielded him common ether instead of a new alcohol. The experiment had been a simple one, its result had not met his anticipations, and it had not even been productive of a new substance; but the nature of his interpretation of the result of it quickly made his name famous with chemists. To begin with, he had seen that his experiment had solved, for him at least, the long-vexed question of the relation of three substances of such fundamental importance in organic chemistry as alcohol, ether, and water, and thereby had determined the true proportions of their atomic quantities or, as we now say, their molecular quantities. It had afforded, besides, a confirmation and proof of the views of Laurent and Gerhardt, comparable to that which was, long after, to be given of the truth of the theory of the periodicity of the elements by Lecoq de Boisbaudran's discovery of gallium. In this way it was destined to do more than anything else in showing how futile was any further opposition by the old school of chemists to the adoption of Gerhardt's system of equivalent quantities now known as molecular quantities. Next, it gave Williamson the basis of his theory of etherification, in which is contained the origin of chemical dynamics, the theory of ionisation, the theory of catalytic action, and the grounds for

reconsidering Berthollet's law of mass action, which had fallen into neglect. Lastly, but perhaps before all in ultimate importance, it led Williamson to form his theory of the constitution of salts, in which is included the foundation of the doctrine of valency and the linkage of radicals.

Some account of his experiment must be given, in order to make his theory clear. He had converted some alcohol partly into ethyl iodide and partly into potassium ethoxide (or ethylate), the former being reconvertible to alcohol by means of moist silver oxide, and the latter by merely dissolving it in much water. He then found that these substances interact with each other in proportions derived from equal quantities of alcohol, and that the products are the substances, ether and potassium iodide. Either of these is derived from both ethyl iodide and potassium ethoxide, and therefore its quantity is chemically equivalent to that of the ethyl iodide or that of the potassium ethoxide. But the two reacting substances are each equivalent to the quantity of alcohol from which they are derived. From this it follows that *two* equal quantities of alcohol are concerned in the production of ether, and that the quantity of it produced is equivalent to either of the two quantities of alcohol. Nowadays, for equivalent the word molecule is used, but the sense is unaltered. Williamson's experiment would doubtless by itself not have proved convincing to many chemists at that time. They would have met it with the apparent contradiction afforded by the fact that alcohol is decomposed into ether and water, in quantities together equal to it in weight and composition, when it is run into sulphuric acid already mixed with alcohol and water in such proportions as to allow the heated mixture to boil at 140°. For, from this fact it would seem just as reasonable to assume that the alcohol, which decomposes into equivalent quantities of ether and water, is itself equivalent in quantity to that of either of its educts, as it is to assume that the ether produced in Williamson's own experiment is but one equivalent or molecule instead of two. But Williamson's papers forestalled in two ways the bringing in of this fact as adverse evidence; first, by the accounts of other experiments which they contain, and, secondly, by the theory of etherification put forward in them. It is important, however, that it should be recognised that the result of his single experiment is really sufficient to establish his point. That experiment in itself indicates that, in the ordinary ether process, there are to be recognised *two* molecules, two equal and distinct quantities, of alcohol which, by their mutual exchange of ethyl and hydrogen, give rise to the ether and water, one molecule of each.

The results of Williamson's other experiments strengthen the argument, but are themselves unconvincing if the result of his first experiment is so. One set of these experiments, in which he prepared mixed ethers, such as methyl ethyl oxide, consisted in letting the iodide derived from one alcohol interact with the potassium derivative of another alcohol. The other set was made up of those in which, in different ways, the mixed ethers are obtained, by using two different alcohols in carrying out the ordinary or continuous etherification process by means of sulphuric acid.

The production of mixed ethers, substances which prove themselves by their composition to be derived from the two alcohols used, shows the propriety of regarding ordinary ether as being all derived from both the ethyl iodide and the potassium ethoxide, instead of half of it coming exclusively from one of these substances and half of it exclusively from the other. Their production served another purpose, because Williamson had found that the same mixed ether was produced, whichever of the two alcohols was used as the potassium or as the iodine derivative. For, from this fact it follows almost necessarily, that the ethers are oxides of two hydrocarbon groups and not of a complex of the two. Williamson has not indeed expressed his views in this way, but as he started his experiments under the belief that the hydrogen of alcohol is or may be all united directly to the carbon, herein following Berzelius, he must have been influenced by some such reasoning when he represented alcohol as the oxide of ethyl and hydrogen, and ether as the oxide of two atoms of ethyl.

The molecular weights thus found by Williamson for alcohol and ether were the same as those assigned to them by Gerhardt on the assumption that molecular quantities of different substances have the same volume in the gaseous state under like conditions. They therefore gave such support to Gerhardt's views as to weaken greatly, as was just now said, the doubts entertained as to the substantial correctness of these views. Other experimental verifications, as is well known, quickly followed, so that in a few years Gerhardt's assumption led to the revival in full force of the rule or hypothesis of Avogadro which, at the time of Williamson's experiments, was well-nigh forgotten, so little had it appealed to chemists for want of sufficient experimental support. It was also largely due to the effect produced by Williamson's experiments and the interpretation he gave of them that the notion of molecules as being the true equivalents, and of their component atoms as being subordinate to them, obtained general acceptance, a notion for the conception of which chemistry is also indebted to Avogadro.

Catalysis or Contact Theory.—When Williamson made his famous experiment there were in the main two views current as to the nature of the process of making ether from alcohol by means of sulphuric acid. Mitscherlich's view, upheld by Williamson's colleague, Graham, was that by contact with hot sulphuric acid (or perhaps by contact with sulphovinic acid), and by virtue of a catalytic force rather than by the influence of any play of chemical affinities, the alcohol decomposed into water and ether, the catalysing acid, whichever it was, remaining chemically unchanged. The other view was that the production of ether was due to decomposition, by heat, of sulphovinic acid (ethyl hydrogen sulphate) into sulphuric acid and ether, followed by the production of fresh sulphovinic acid by the union of alcohol with sulphuric acid. This view was Liebig's, in whose laboratory Williamson had been trained. Both accounts were made up of facts, hypothesis, and error; neither could be dignified with the name of theory, for neither offered any sufficient explanation. In propounding his theory, the one and only theory that has

been framed, Williamson was careful repeatedly to point out that he was combining the theories of his two eminent seniors in his own, but it is clear that the enunciation of his own theory implies the rejection of the essential points in both of their theories. The catalytic phenomenon is a patent fact; but the existence of a catalytic force, and the activity of a contact which brings about chemical change without the contact substance being affected, are both to be cast aside as baseless fancies. The production of sulphovinic acid is also a fact not to be denied; the decomposition of the acid into ether, by heat and by itself, is only imaginary.

Williamson's description of etherification is that a molecule of alcohol reacts with a molecule of sulphuric acid to form ethyl hydrogen sulphate and water, and that then a second molecule of alcohol reacts with this ethyl hydrogen sulphate to become ether and sulphuric acid again, this pair of reactions being ever and again repeated, so long as the conditions are that the ether and water produced are being removed and replaced by fresh alcohol. In this way it is made evident that the quantity of alcohol which gives a molecule of ether and a molecule of water must be treated as being not one but two molecules. Here, it will be seen, is given, for the first time fully (but see p. xxvii) the form of explanation, now universally accepted, of all catalytic action.

Chemical Dynamics.—To complete his theory, Williamson points out that whilst the two double decompositions involved are, in themselves apart, perfectly conformable with others, the fact of their alternations and continuous successions is something obviously independent of the exercise of chemical affinity, and inconsistent with the supposition that the atoms of a compound are in a state of rest. There must therefore be a dynamical treatment of chemical phenomena, in which the degree and kind of motion possessed by atoms must be studied, and the element of time be taken into consideration. The alternating changes of sulphuric acid and sulphovinic acid into each other cannot be attributed to any exercise of superior affinity, for one moment sees replaced by hydrogen the ethyl which during the preceding moment had replaced a hydrogen atom. Nor can it be referred to the action of some occult catalytic or contact force. It happens because the atoms are not at rest and confined within the molecule, but are constantly changing into other molecules, there taking the place of like or similar atoms. In completing his theory of etherification in this way, Williamson, as is universally admitted, placed the dynamical idea of chemistry on a definite concrete foundation. In a lecture on the subject at the Royal Institution, he expressed himself, as follows, in words which recall the opinion pronounced by Robert Boyle in the infancy of the science:—"The dynamics of chemistry will commence by the rejection of the unsafe and unjustifiable supposition that the atoms of a compound are in a state of rest, will study the degree and kind of motion which atoms possess, and will reduce to this one fact the various phenomena of chemical change." In another place in this lecture he says:—"There are many *primâ facie* evidences that time is necessary for

chemical action, but this fact has not as yet entered into the explanation of phenomena."

Ionisation.—It is evident, too, that in the theory of etherification he foreshadowed the modern notion of ionisation. This may be seen in what precedes, but the following quotation seems too interesting as an illustration of the point for it to be omitted:—"A drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH,... each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen or, what is the same thing, of chlorine. . . . Suppose we mix with the hydrochloric acid some sulphate of copper, the basylous elements, hydrogen and copper, do not limit their change of place to the circle of the atoms with which they were at first combined, the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid." More might be quoted with advantage, but what is here given will be enough to show that, whatever may be the ultimate view adopted on the subject of ionisation, Williamson played an important part in the development of the conceptions on which the theory is based.

Mass Action.—Following up his illustration, just quoted, with another in which sulphate of silver is used instead of sulphate of copper, for the sake of the example it affords of the precipitation of an insoluble compound, he refers to Berthollet's view about mass action, and gives new life to it by accounting for the existence of mass action between substances constituted of atoms as an action due to the innate motion of these atoms carrying them from molecule to molecule.

Structural or Positional Formulæ.—In discussing the facts concerned in the production of ether, Williamson showed, for the first time, how chemical formulæ might be so written as to represent chemical constitution as an arrangement and interdependency of atoms, formulæ thus constructed being what are now known as "structural" formulæ. He then developed the subject in papers on the constitution of salts, the anhydrides of monobasic acids, and sulphuryl hydroxychloride.* This method, of expressing by symbols the conclusions to be drawn from the results of experiments as to the chemical constitution of substances, has turned out to be a veritable "calculus of chemical operations," the importance of which to the progress of chemistry can hardly be overestimated.

When Williamson began to publish his views, Gerhardt had already introduced his unitary synoptic formulæ, the nature of which may, perhaps, be best indicated by calling them "agnostic" formulæ. For they were

* "On the Constitution of Salts" (1851); "On Gerhardt's Discovery of Anhydrous Organic Acids" (1853); "Note on the Decomposition of Sulphuric Acid by Pentachloride of Phosphorus" (1854).

formulæ, the purpose of which was to make no vain attempt to indicate chemical constitution, but to express as simply as possible only the ultimate chemical composition of equivalent quantities of substances. Gerhardt and Laurent did not deny that substances do have atomic structure, but they denied that we could expect to make out anything about it. Such notions concerning chemical constitution, as that nitre consists of and contains potash and nitric acid, and that alcohol consists of ether and water combined together, had been shown by them to be unwarranted assumptions, but were still current.

What Willliamson wanted—instead of Gerhardt's synoptic formulæ of reactions, and of the ill-conceived constitutional formulæ which they were intended to replace—were such formulæ as might* be used as an actual image of what we rationally suppose to be the arrangement of constituent atoms in substances, between which decomposition may be effected by the exchange of a radical in the molecule of one substance for a radical in the molecule of another substance. Now, in order to describe, by means of a chemical equation, the process by which the change is effected, in the reaction of one substance with another, that change should be represented by the juxtaposition of the formulæ of the reacting substances, and by then indicating in these formulæ what takes place in the interchanging substances. The adoption of such a method necessitates a reference to types, from which, by the replacement of certain elements or radicals, the constitution of substances of increasing complexity can be deduced.

Williamson took the constitution of water to be the structural type of salts and of classes of substances apparently allied to them, and constructed formulæ for water and for each of these substances in which the three symbols or, in case there were more, three groups of symbols, are so spaced out as to represent by their relative positions always the same structural relation, whatever that may be, in each of them. Thus

$$\begin{matrix} H \\ H \end{matrix}O, \quad \begin{matrix} H \\ K \end{matrix}O, \quad \begin{matrix} K \\ K \end{matrix}O, \quad \begin{matrix} NO_2 \\ K \end{matrix}O, \quad \begin{matrix} NO_2 \\ H \end{matrix}O, \quad \begin{matrix} NO_2 \\ NO_2 \end{matrix}O,$$

are his formulæ for water, caustic potash, potassium oxide, nitre, nitric acid, and nitric anhydride. Similarly, to alcohol, ether, acetic acid, acetic anhydride, and ethyl acetate, he gave the formulæ

$$\begin{matrix} H \\ C_2H_5 \end{matrix}O, \quad \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}O, \quad \begin{matrix} C_2H_3O \\ H \end{matrix}O, \quad \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}O, \quad \begin{matrix} C_2H_3O \\ C_2H_5 \end{matrix}O.$$

These triangulated formulæ are now usually unfolded into straight-line formulæ, thus

$$HOH, \qquad KO(NO_2), \qquad (C_2H_5)OH, \qquad (C_2H_5)O(C_2H_3O);$$

but are otherwise unaltered.

The Linkage and Valency of Radicals.—It was the significance given by Williamson to the relative *position*, to the "juxtaposition," of the three

* The next 11 lines are almost in Williamson's own words.

symbols or groups of symbols, which constituted the essential novelty and the importance of these formulæ as constitutional formulæ. It is clear what that significance was to him. For instance, as regards alcohol, it was that one-sixth of its hydrogen is "held" united to the carbon and rest of the hydrogen by its atom of oxygen; that in potassium acetate, half the oxygen serves to "hold together" the potassium with the rest of the salt. Again, sulphuric acid is a dibasic acid, *because* the radical sulphuryl (SO_2) holds together two atoms of hydroxyl. Carbonyl (CO) is given by him as another example of a radical which, in the carbonates, replaces two atoms of the hydrogen of a doubled molecule of water, and thus holds together the two substituted water residues or metalloxyls, thus, $\frac{KO}{KO}CO$.

Thus was enunciated for the first time the fundamental part of the doctrine of the linkage of atoms and the valency of radicals. Later on, he gave experimental evidence that sulphuryl is bivalent in sulphuric acid, of the same convincing kind as that he had given of the bivalency of oxygen in alcohol, ether, and water. It consisted in the application of the discovery he had made of sulphuryl hydroxychloride, and of its production from sulphuric acid by means of phosphorus pentachloride (p. xxxvi). In his description of this production, he showed himself already (1854) discarding anything there might be in the presentation of the water type which is outside this theory of the existence and linking power of multivalent radicals. Again (later in 1854) he showed the same thing, when he pointed out that the remarkable substance, ethyl orthoformate, "may be equally well conceived to be a body in which the (oxylic) hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform, as (to be) one in which the chlorine of chloroform is replaced by peroxide of ethyl (ethoxyl)."

Confining, as he did, his attention to the water type, the only elemental atom or radical he exhibited, as exercising linking power, was oxygen. Odling and, pre-eminently, Frankland extended the conception to several other elements, but it was not till Kekulé recognised that, in the case of carbon in organic compounds, atoms of the same element may be united directly together, that the real and supreme value of Williamson's conception became evident, and the reference to compound radicals and types to be no longer necessary.

Gerhardt added three other types to Williamson's water type, but all were to him no more than "types of double decomposition," and wanted therefore that structural significance which they had for Williamson.

Just as the latter was led by his water-type formulæ to differentiate one atom of the hydrogen of alcohol from the other five, so was he quickly afterwards led to separate the oxygen of acetic acid into one atom as being that of water, and the other as being within the radical, acetyl (his "othyle"). This procedure was at once justified by the discovery (by a method similar to that employed by Williamson in connection with ether)

of the monobasic acid-anhydrides by Gerhardt, who had himself previously deemed their existence impossible.

To bring out the fact more strongly that Gerhardt's type formulæ were no anticipation of Williamson's structural formulæ, it may be here recalled to mind that, in 1863, Playfair advocated the reference of salts to the type of hydrogen peroxide as more appropriate than Gerhardt's reference of them to the type of water, giving a sufficiently plausible presentation of the subject, quite worthy of consideration until the views of Williamson as to atomic structure are applied to show the futility of Playfair's proposal. It is of interest to note further that Gerhardt, before Williamson had worked upon etherification, had gone so far as to regard ether and alcohol as the normal and acid esters of water, water being treated as a dibasic acid, and yet had wholly missed the point of the relationship afterwards brought out and formulated by Williamson. Gerhardt wrote the formulæ of ether and alcohol as $(C_2H_4)_2,OH_2$ and $C_2H_4,OH(H)$, in order to represent this view of their relationship. These instances from Gerhardt's writings serve to illustrate how entirely original were Williamson's notions concerning the chemical constitution of salts and other substances.

Kekulé, who spent the session 1853–54 in Stenhouse's laboratory at St. Bartholomew's Hospital, and passed much time in intimate companionship with Williamson, carried out at that time a research* on thiacetic acid, which afforded a beautiful confirmation of the correctness of Williamson's action in formulating acetic acid with half its oxygen in the radical, acetyl or "othyle." Kekulé showed that by acting upon acetic acid, or its anhydride, or its ester, with phosphorus tersulphide or quinquesulphide, compounds were produced in which only half the oxygen was replaced by sulphur and which had much resemblance to the original acetic compounds.

Substance Distinct from Radical of same name.—Concerning the radicals which he introduced into chemistry, such as sulphuryl and acetyl, and others such as ethyl, the existence of which he accepted, Williamson was careful to point out that they are not to be confounded with the substances or bodies in the free state, which would be indicated by the same names and formulæ. Extending this important distinction, too often still neglected, to metallic and other elemental radicals, he wrote:—"To say that metallic zinc is contained in its sulphate is an expression authorised by usage, but is only strictly true by abstraction from most of the properties of the metal. The material atom which, under certain circumstances, possesses the properties which we describe by the word 'zinc' is no doubt contained in the sulphate but with different properties, and in the chloride with properties different from either; so also of the compound radicals."

Sulphuryl Hydroxychloride; Dibasic Acids† (see p. xxxv).—In spite of the work of Laurent and Gerhardt, the majority of chemists at that time still preferred to consider potassium sulphate as a salt which, like nitre, contains

* 'Roy. Soc. Proc.,' 1854—5, vol. 7, p. 37.

† "Decomposition of Sulphuric Acid by Pentachloride of Phosphorus," 1854.

only one atom of potassium, and the acid salt as being potassium sulphate in combination with sulphuric acid. Williamson now placed it beyond dispute that, just as potassium hydrogen sulphate is intermediate to potassium sulphate and sulphuric acid (hydrogen sulphate) in there being replacement of hydrogen by metal or the reverse, so sulphuryl hydroxychloride is intermediate to sulphuryl chloride and sulphuric acid (sulphuryl hydroxide), in the interchange of hydroxyl and chlorine:—

$HO(SO_2)OH$,	$HO(SO_2)OK$,	$KO(SO_2)OK$
$HO(SO_2)OH$,	$HO(SO_2)Cl$,	$Cl(SO_2)Cl$.

Gerhardt, who had just then prepared chlorides of dibasic acids, had not succeeded in bringing his facts into line with the theory of monobasic acids, which he had adopted from Williamson. The latter's discovery of the substance intermediate to sulphuric acid and its chloride (sulphuryl chloride), and his recognition of its nature as such, rendered evident how this was to be done, and demonstrated the fullness with which the water-type theory met the case. In this way, a material impulse was given to the general adoption of structural or valency formulæ.*

In 1854, several papers upon subjects worked out in his laboratory by assistants and other students, all bearing the impress of his directing mind, were brought by Williamson before the Royal Society. Some of them are of great interest, but space cannot be given for notice of them here. Also, in this year, he read a note before the Royal Society on the magnetic medium.

In 1855, when Graham resigned the Chair of Chemistry in University College on becoming Master of the Mint, Williamson was unanimously chosen in his place, the Senate having decided, at Williamson's strongly urged wish, to combine the Professorships of Chemistry and Practical Chemistry in one person. His researches on bleaching salts and on Prussian blue had gained him his first professorship; now, it was those upon etherification which contributed very largely to his success in getting the second and higher appointment. These researches had just before led to his being made a Fellow of the Royal Society. Three weeks after he had obtained his new position he married Emma Catherine Key (third daughter of his colleague, Professor T. H. Key, F.R.S., also Head Master of University College School), to whom he had been engaged for more than a year. In 1857, he was for a month almost deprived of sight by an explosion in the laboratory.

The session ending with his appointment to the Professorship of Chemistry was the last in which Williamson published papers upon the results of researches by himself, or carried out at his instigation, with the notable exception of those by Sakurai, in 1880–81. This abstention from research work, however greatly to be regretted, is not perhaps much to be wondered at. His mind, indeed, at this time and for years afterwards, teemed with suggestions which, had they been carried out with his own hands, would no

* Williamson's papers on Etherification and the Constitution of Salts have been republished in the convenient form of an Alembic Club Reprint (16).

doubt have sometimes been fruitful of results though not always those expected. But having to be left to others, competent though they probably were, the facts reached generally caused him to discontinue the pursuit of one idea for that of another, so that a research was rarely brought to a satisfactory conclusion. The same may be said of his later attempts in the applications of chemistry, carried on at his Willesden works.

His professorial position made, indirectly, great demands upon his time. He took an energetic interest in the affairs of University College, among other things in forwarding through it the movement to get the University of London to grant Degrees in Science. On the Council of the Chemical Society he served continuously from 1850, becoming President in 1863; and he took a prominent part in the then somewhat frequent and elaborate discussions at its general meetings. In 1859 he began his first term of office on the Council of the Royal Society. In all co-operative work his opinions had great weight with his colleagues and others, in consequence, apparently, of the extent to which he at once saw through difficulties, and of his not being dismayed by opposition. Indeed, as a strenuous advocate of any cause he took in hand, he was always a force to be reckoned with, in movements to be undertaken in which he might be interested. He generally came to occupy a forward, if not the front, place in such a movement.

Williamson was one of the most hospitable of men, and after his marriage was seldom without one or more friends at his table. He frequently entertained foreign guests, among whom may be mentioned J. P. Cooke, Wurtz, Berthelot, Cornu, and Cannizzaro. Everyone at once felt at home with him and Mrs. Williamson, both blest with the most kindly dispositions.

There is yet another reason, and no doubt the essential one, for his comparative neglect, from this time forward, of the field of chemical research, hitherto so brightly illumined by him. From 1854, for several years to come, his mind became occupied with the possibility of generating steam for mechanical purposes in a more satisfactory way than was then being followed. By 1859 he had invented a water-tube boiler, or "tubulous" boiler as he suggested it should be called, to distinguish it from the common form with the fuel gases passing along tubes through the water. He then wrote of his invention as important and as fast approaching completion. Again, in 1862, he called it the best and most important work in his life. This was just after he had taken out letters patent for it. The claim in his patent runs, with slight abridgment, as follows: "The construction of boilers wherein a number of slanting or vertical tubes, each acting as a separate steam generator, are firmly connected to a foundation at their lower ends, and are there made to intercommunicate by having connecting pipes attached to them for supplying the feed water, whilst the upper ends have no rigid connections, and are free to expand in the direction of their length, the steam being conducted, by small curved pipes attached to their upper ends, into main steam-pipes." Stacks of such pipes formed the side-walls of the combustion chamber, and allowed the hot gases to circulate

round the pipes, so as to raise steam and superheat it. As to what extent Williamson's invention is to be considered as an anticipation of the water-tube boilers now in use with marine engines, it is beyond the competence of the present writer to offer an opinion.

Early in 1863, writing to his father, he referred to his patent and appealed for further pecuniary assistance. His father showed himself unsympathetic and refused help, advising him to leave the invention alone and devote all his abilities to the duties of his professorship.

Towards the end of that year (1863) Williamson received from Mr. Hugh Matheson, of Lombard Street, an offer to send him five young Japanese to be boarded and looked after in matters concerning their education. He was unable to take in more than three of these as boarders, but undertook the general supervision of the education of them all. These young men were destined soon to play important, in some instances most important, parts in the great and practically bloodless revolution whereby the Imperial House of Japan was restored to power, and the country led to adopt and build upon much that it found good in European arts and sciences, forms of government, commerce, manufactures, and education. One of these, now the Marquis Ito, framed the present Constitution; a second, (now Count) Inouye, gave direction to the development of commerce; a third, also named (Viscount) Inouye, established the railway system; and a fourth, (Viscount) Yamao, acting as the first Minister of Public Works, introduced, with the aid of instructors from this country, a system of technological training which has proved to be eminently successful.

Later on, the Prince of Satsuma sent over a party of 16 young Japanese to be placed under Williamson's care, among them being Mori, who became Minister Plenipotentiary both to London and New York, and afterwards a member of the Cabinet in Tokyo. Also of the number, and later on representing their country abroad, were Yoshima and Sameshima.

Williamson took a keen interest in all the work of these pioneers and some of their successors in the development of Japan on the European side of its life. Particularly was he responsible for the selection of the staff of professors to whom was to be entrusted the planning of the technological education of the country. Several letters are still preserved which show how highly were appreciated the efforts made by Williamson in the cause of education in Japan, both through the instrumentality of the statesmen for some time in his charge, and afterwards also in other ways.

In conjunction with Dr. W. J. Russell, Williamson made and perfected, in 1857 to 1864, a great improvement in the analysis of gases by devising the "pressure tube," in which is enclosed over mercury a quantity of air which has its normal volume when the surface of the mercury in the tube stands at a certain mark on the tube. Any gas to be measured being made to stand over a column of mercury of the same height in a tube by the side of the pressure tube, its volume evidently becomes the same as it would be under normal temperature and pressure. By the use of the pressure tube,

therefore, the necessity of correcting for atmospheric pressure and temperature is avoided and the process of analysis greatly facilitated. A preliminary notice of the apparatus appeared in the 'Proceedings of the Royal Society' for 1857, but it was not fully described in an improved form until 1864 in the 'Journal of the Chemical Society.'

Williamson's courses of lectures to the students of University College were always of an impressive, suggestive, and interesting character, in spite of the fact that he did not do much to modify them as time went on, in order that they should continue to reflect the rapid developments which chemistry is ever undergoing. He used to say that he had come to look upon his early lecturing as having been much too elaborate and advanced, and to believe in the wisdom of greatly simplifying his teaching. A small text-book published by him, in 1865, served to illustrate what his notion was as to the ground to be covered by a general course of lectures. The courses of practical chemistry, entailing as they did hard work and continuous attention, he had after a few years to leave to be given by his assistants, several of whom have since become eminent. He was emphatically a great teacher, honoured and revered by his pupils.

Williamson gave several lectures at meetings of the Chemical Society: in 1855, on certain processes for the decomposition of fats by water at high temperatures; in 1859, on gas analysis; in 1861, on thermodynamics in relation to chemical affinity; in May, 1864, on the classification of the elements according to their atomic weights; in December, 1864, on chemical nomenclature and notation; and in 1869, on the atomic theory. The last three of these are contained in the Journal of that Society. The subject of the classification of the elements had suggested itself to him through the proposal of Cannizzaro to readopt most of the atomic weights used by Berzelius. Cannizzaro had based his proposal mainly on physical grounds, and Williamson proceeded to summarise the chemical evidence in support of Cannizzaro's system of atomic weights.

In this lecture there occurs Williamson's statement of the grounds for rejecting Kekulé's contention that the atomic valency of each element must be constant. Thoroughly convinced as to chemical valency being variable, Williamson did not hesitate some years later in his address to Section B of the British Association in 1881, and elsewhere, to enlarge the notion in applying it to the multivalency of the dominant element in metallic double salts. He thus, to some extent, anticipated Werner's conception of the "co-ordinating" power of such elements. Representing by symbols the well-known alkali double salts of auric and platinic chlorides as compounds of quinquevalent gold and octovalent platinum, $AuCl_4Na$ and $PtCl_6K_2$, he pointed out the converse analogy of the former with sal-ammoniac, NH_4Cl, explaining that the atom of sodium is not to be regarded as directly united with the atom of gold, but indirectly with it through the chlorine.

The lecture on chemical nomenclature and notation appears to have been

given after the attempt at agreement, by a committee of Section B of the British Association appointed to consider the subject, had failed. His recommendations were largely adopted by chemists, and are followed even now to some extent.

Williamson was a convinced believer in Dalton's atomic theory, and held that the results of modern research sufficed to prove its truth. Giving his lecture on the atomic theory from a handful of unarranged notes, he filled the whole time of the meeting with an eloquent assertion of the truth of the theory, holding his large and distinguished audience in unflagging attention. After the summer vacation, another meeting was given up to the discussion of the subject of the lecture. It was a memorable and interesting evening in the life of the Chemical Society. Both lecture and discussion are reported at length in the *Journal*, but the reports give no adequate reproduction of what was said. Frankland, Brodie (in the chair), Allen Miller, Tyndall, Carey Foster, Odling, Mills, C. R. A. Wright, and others took part in the discussion, and the excitement ran high at times. But nothing came of it all, and chemists remain not much less divided on the subject now than they were then.

In 1862 Williamson was the recipient of one of the Royal medals, awarded by the Royal Society in recognition of his work on etherification. In 1863–4 and 1864–5 he was President of the Chemical Society, the latter being the year in which he delivered two of the lectures just noticed. He was again President of that Society in 1869–70 and 1870–71. He had thus the opportunity of inaugurating the Faraday Memorial lectures, of which the first was given in 1869 by Dumas. The next year he made "perhaps the most memorable year in the history of the Society," by starting the publication, in its *Journal*, of monthly reports in the form of abstracts of all papers of a chemical nature, "a work second only in importance to that accomplished by the establishment of the Society. No steps could have more directly promoted the main objects of the Society."

Soon after 1870 he established at Willesden some experimental works for improving and inventing chemical manufacturing processes, and continued them for about eight years. Although his outlay must have been considerable, he arrived at no profitable results. Among other things, improvements in the manufacture of sodium hydroxide are said to have been tried. He also attempted the economic recovery of gold, platinum, and other rare metals from pyrites, by roasting with salt and in other ways.

In 1863, at Newcastle, he presided over Section B of the British Association, his address being upon recent progress in chemistry. He was President of the British Association itself in Bradford, in 1873, taking for the subject of his address the meaning and use of scientific activity and what can be done to encourage it for the advancement of science. He used chemistry to illustrate his views, and gave the atomic theory as the basis of its development and wonderful progress. He again presided over Section B of the British Association meeting in York, in its Jubilee year in 1881, in

order that he might trace in his address the history of chemistry since the foundation of the Association, in accordance with the plan of giving that year in each of the sections a history of the science with which it was concerned. From 1874 to 1891 he was the General Treasurer of the British Association.

After serving on the Council in 1859–61 and in 1869–71, Williamson was made Foreign Secretary of the Royal Society in 1873, and continued to hold that office till 1890. He was a particularly able linguist. His earlier papers on chemistry were written by him in German, being intended for but not published in Liebig's *Annalen*, and then translated into English for publication in the Memoirs of the Chemical Society.

In 1876 he was appointed by Sir C. Adderley to succeed Dr. Letheby as Chief Gas Examiner under the Board of Trade.

The Birkbeck Laboratory of University College had for many years proved quite insufficient for the needs of the various classes, to which had been added those in Applied Chemistry. The laboratories now in use were therefore put up under Williamson's direction, and he moved into them in 1880. In this year also a research was carried out under his direction, which was interesting not only on account of its results, but of the Japanese nationality of its author, and of the part which Williamson had already taken in promoting the spread of scientific knowledge in Japan. The research was by Sakurai, now well known to chemists, and eminent in Japan among University professors. He published three papers in the 'Journal of the Chemical Society' on the subject of metallic compounds of multivalent hydrocarbon radicals, two of which were worked out in University College laboratory and the third in Japan. The monomercuric iodide derivative of methane was already known, but Sakurai unexpectedly succeeded in obtaining the compounds,—$CH_2(HgI)_2$, $CH(HgI)_3$, (the metallic analogue of chloroform, $CHCl_3$), and other derivatives which as compounds of bivalent and tervalent radicals were of a new order.

During 1884 and 1886, Williamson took an active part in the discussions about a teaching university for London.

In 1888 he resigned his active appointments at University College where he had been a professor for 39 years, and was elected Emeritus Professor of Chemistry. A portrait of him, by Collier, which hangs in the Council Room of University College, was presented on behalf of the subscribers by Sir Henry Roscoe. Another portrait, painted by Mr. Biscombe Gardner, was presented, 10 years later, to the Chemical Department of the College. A short time before his retirement, that is, in 1886, he had gone to live at High Pitfold, Haslemere, and there began to devote most of his time to farming on scientific principles, only now and then visiting London, but much enjoying the occasional visits of his children and grandchildren to Haslemere. Very slowly his health began to decline, and from this cause he had to absent himself from the Jubilee Meeting of the Chemical Society in 1891. Seven years later, however, he was able by a great effort to attend

a banquet given by the Chemical Society on November 11, 1898, to him and the five other Past Presidents, who had then been Fellows of the Society for at least 50 years. He not only attended the dinner, but spoke, as did his colleagues, to the toast of the evening. The President (Professor Dewar) spoke of his services to chemistry in glowing terms. A seniority of four months in Fellowship of the Society made Professor Odling's turn to speak precede Williamson's, who was in years considerably his elder, and Odling made happy use of the opportunity to refer to his brother guest. He said, "I have always looked upon myself . . . . as a follower of Williamson. It has been my pride to reckon myself one of his adopted pupils—a disciple of his ideas more perhaps than many of those who were his actual pupils. He was always very decided in his notions. Sometimes, indeed, I turned a little restive, but was always soon pulled up into form again—sometimes more abruptly, perhaps, than was quite agreeable at the moment. At one time I laboured under the sad suspicion of being a little unsound as to the Atomic Theory."

In 1901 Williamson gave up his office of Gas Referee under the Board of Trade, his health having then utterly broken down. He died in May, 1904, eighty years old, and was buried at Brookwood, in Surrey. Besides his widow, closely associated with him for half a century in almost every incident of his public and private life, with its many hospitalities, his daughter, Mrs. Fison, and her three children, and his son, Dr. Oliver Key Williamson, survive him.

Williamson was Ph.D. (Giessen); LL.D (Dublin and Edinburgh); D.C.L. (Durham); Hon. F.R.S.E.; Fellow of the University of London; Hon. M.R.I.A.; Hon. Member of the Literary and Philosophical Society of Manchester; Hon. Member of the German and American Chemical Societies; Corresponding Member of the French Institute (Academy of Sciences); Corresponding Member of the Royal Turin Academy of Sciences; Extraordinary Member of the Accademia dei Lincei, Rome; Extraordinary Member of the Royal Berlin Academy of Sciences. He was a Member of the Athenæum Club, elected by the Committee without ballot.

To know Williamson was to love him for his truly affectionate disposition. He was a true and constant friend. But there were many acquainted with him who never got to know him. There was a reserve about him which seemed to turn away advances and which made him appear indifferent to forming new friendships. This reserve, however, was all unreal and its appearance wide of the truth. His manner was largely attributable to his near-sightedness, which, firstly, in his youth led him to find his own company sufficient, and which, secondly, interfered always with that ready recognition of persons and faces which is necessary for the full enjoyment of social life. Far from being really reserved, he had an open and most sympathetic disposition. But, again, to his cost, he was an outspoken, severe, and caustic critic of doctrinal views in chemistry, and in this capacity he seemed to repel men of softer mould. It was always the doctrine he was hard upon, never the man who, to him, was foolish enough to hold it. Of no one

was he a keener critic than of himself, and it was at times disconcerting to his followers to hear him dilate upon the weakness and uncertainty attaching to views which he was himself habitually defending. To some he seemed not to brook contradiction. It was not really so; he was only the strenuous advocate, and, however discomposed he felt for the moment, he gave and received blows without any trace of personal ill-will.

E. D.

SIR WILLIAM JAMES LLOYD WHARTON, 1843—1905.

William James Lloyd Wharton, second son of Mr. Robert Wharton, County Court Judge of York, was born in London on March 2, 1843. In August, 1857, having been previously educated at Burney's Academy, Gosport, he entered the Royal Navy on board H.M.S. "Illustrious," at that time recently commissioned as a training ship for Naval Cadets, stationed at Portsmouth. Passing out of the "Illustrious" with great credit, he was appointed midshipman of H.M.S. "Euryalus" in April, 1858, on board which ship Prince Alfred, afterwards Duke of Edinburgh, was also serving. In November, 1860, he was appointed to H.M.S. "Jason," and, while serving in her on the North American and West Indies Station during the summer of 1861, he was lent to H.M.S. "St. George," employed on fishery duties in Newfoundland. Having completed his time as midshipman, on January 13, 1863, he passed his examination in seamanship for the rank of lieutenant. The "Jason" returned to England to pay off at the close of 1864, Wharton having received his commission as Acting Lieutenant of her two months previously. He now had the opportunity of completing the necessary qualifying examinations in gunnery and navigation, in which he acquitted himself brilliantly, and was confirmed in his rank March 15, 1865. In December he was awarded the Beaufort Testimonial for passing the best examination of the year in Mathematics, Nautical Astronomy, and Navigation.

In the meantime, in July, 1865, he had been appointed to H.M.S. "Gannet," a sloop commissioned partly for the general duties of the fleet and partly for surveying service on the North American and West Indies Station, but acting entirely under the orders of the Commander-in-Chief. In that ship he acquired his first experience in the work to which his life was afterwards devoted, showing great ability and aptitude for surveying duties, and receiving the commendation of the Board of Admiralty for the zeal displayed by him in the work performed in the Bay of Fundy. The "Gannet" paid off in November, 1868.

The Commander-in-Chief, Vice-Admiral Sir James Hope, had already realised Wharton's abilities, shown as much by his practical work on board

the "Gannet" as in the distinction he had gained in passing his examinations; consequently, when the Admiral was about to hoist his flag at Portsmouth, Wharton was offered the appointment of Flag-Lieutenant. The Hydrographer meanwhile had promised to submit his name as 2nd Lieutenant of H.M. Surveying Vessel, "Newport," and Wharton, considering himself pledged to the surveying service, was prepared to forego Sir James Hope's offer, although he was fully aware he would thereby sacrifice the prospect of certain promotion at the end of three years. Fortunately, however, Sir James Hope took another view, and, speedily arranging matters with the Hydrographer, Wharton was appointed as his Flag-Lieutenant on March 1, 1869. Whilst so employed he wrote "The History of H.M.S. 'Victory,'" which still commands a steady sale to the public, the proceeds being devoted to the Royal Naval Seamen's and Marine Orphans' Home, Portsmouth.

H.M.S. "Urgent" being temporarily commissioned in November, 1870, to convey a scientific expedition to the neighbourhood of Gibraltar to observe the forthcoming total eclipse of the sun, Lieutenant Wharton was gratified at being appointed to her as 1st Lieutenant for the cruise.

On March 2, 1872, he was promoted to Commander on Sir James Hope striking his flag, and the following month was appointed to the command of H.M. Surveying Vessel, "Shearwater," on the Mediterranean Station, and afterwards on the East Coast of Africa. His work in the Mediterranean was chiefly distinguished by a valuable contribution to Science in the form of an investigation of the surface and undercurrent in the Bosphorus, setting at rest the many controversies respecting the exhaustless flow of water from the Black Sea to the Sea of Marmora by proving that an undercurrent existed as strong as that on the surface, but which invariably flowed in exactly an opposite direction.

His report, which was officially published, may be considered as prescribing the method for similar enquiries.

Whilst at Rodriquez, in the South Indian Ocean, he took part in observing the transit of Venus in 1874.

The "Shearwater" was paid off in July, 1875, and in June the following year he commissioned the "Fawn" for surveying service in the Mediterranean, Red Sea, and East Coast of Africa. Starting with a staff of officers, most of whom were wholly inexperienced, Commander Wharton set himself to train them after his own ideals, and succeeded in imbuing his assistants with something of his untiring energy and love of the work. Whilst exacting the utmost that each individual was capable of giving to the service, he exercised unremitting patience and forbearance, and, throughout a prolonged commission of four and a-half years, endeared himself to all who had the happiness to serve under him. He was sympathetic and considerate towards both officers and men, and entered heartily into all schemes for their recreation when opportunity offered. This commission of the "Fawn" was perhaps one of the most successful, as it certainly was one of the happiest, ever spent by a surveying vessel in modern times. The last two

years were occupied with the survey of the Sea of Marmora, an excellent piece of work for which he and his officers received an expression of the approbation of the Lords of the Admiralty.

On January 29, 1880, Wharton was promoted to Captain, and the "Fawn" was paid off at Malta at the end of the year.

"Hydrographical Surveying" was written by Captain Wharton during the interval of leisure which now followed, and immediately on its publication it was recognised as the standard work on the subject. As such it is still in use in both British and Foreign navies, its value being thus well proved despite the characteristically modest tone of its author's preface.

In March, 1882, Captain Wharton commissioned H.M.S. "Sylvia," for surveying service in the River Plate and Straits of Magellan. He successfully observed the transit of Venus for the second time in December that year. The work in the Straits of Magellan was pushed on rapidly in spite of hardships and difficulties which had to be encountered, with the result that the survey was completed within the allotted time, but two seasons' work carried on in such an inhospitable climate, and in such dangerous waters as the western part of the Straits of Magellan, told so considerably upon Captain Wharton, that during this time he aged much in appearance. Before he left England it had been an open secret that on the retirement of Sir Frederick Evans, Captain Wharton should succeed him as Hydrographer of the Navy.

On the return of the "Sylvia" to Montevideo in March, 1884, it became necessary therefore that he should leave the ship and proceed to England by mail steamer. On August 1, 1884, he was appointed Hydrographer, at an age younger than that of any officer preceding him in the office. This closed his career afloat.

Wharton's administration of the hydrographic department of the Admiralty continued uninterruptedly for 20 years with constantly increasing credit, and to the great advantage of our own Navy, as well as of the whole maritime world. This period covered the enormous expansion that took place both in the *personnel* and *matériel* of the Fleet, causing corresponding accessions to the labour of departmental work. During the same period the number of chart-plates was largely increased, and the number of charts printed annually for the Fleet and for sale to the public multiplied threefold.

Gifted with an extraordinary capacity for work, Wharton never spared himself; the sound judgment, and wide scientific attainments, which he constantly brought to bear upon the infinite variety of subjects with which he was daily called upon to deal, secured for him the respect and confidence of successive Boards of Admiralty, to whom he was an ever true and inestimable adviser in all matters hydrographic.

Not the least important part of his work at the Admiralty was the advice he was called upon to give on naval engineering works generally, and particularly on the great engineering schemes which have been proceeding during the last ten years under the Naval Works Acts.

In dealing with such questions, his clearness of thought, the breadth of his general knowledge, his keen appreciation of engineering difficulties, and his broad and far-seeing view of Naval requirements were of the utmost value in framing the general lines of the schemes, as well as maturing their details. Always willing to give his advice and assistance to his colleagues at the Admiralty, his general remarks and criticisms afforded information of the greatest value to them, and in general conversation on professional subjects all those with whom he was brought in contact could realise how wide his knowledge was.

The part he played in settling the main principles upon which the Naval Defences of the country are now based can only be known to and appreciated by those with whom he was associated at the time.

It was one of his marked characteristics that the mass of information he had acquired on all sorts of subjects was at once available on the spur of the moment. No matter what difficult question might arise in any part of the world, he was ever ready with the proper answer; yet although his mind was such a storehouse of valuable and instantly available knowledge, he remained to the last the same simple and modest sailor as he began.

As ex-officio member of the Meteorological Council he attended its meetings assiduously and rendered important service to the advancement of Ocean Meteorology.

His personal interest in the surveying service was unceasingly manifested in the voluminous semi-official correspondence he maintained with the officers in command of surveys. Scientific subjects of every kind bearing on hydrography always claimed his attention. His strong desire was ever to make his work thoroughly scientific, and to ensure that the same ideal was kept before the surveying officers of the Navy. Thus he took great pains to have a new and revised edition of the 'Admiralty Manual' prepared, and he sought as coadjutors in this task the most distinguished and experienced men of science in each branch of investigation treated of in that excellent work. So anxious was he to furnish the surveying staff with all the available assistance in their work that he applied to the Director-General of the Geological Survey for a list of the more typical and frequently recurring minerals and rocks, and he had a series of collections of specimens made and distributed among the surveying vessels. He wished that every naval officer, besides being thoroughly trained to do the official work entrusted to him, should be taught to use his eyes in observing Nature, and be encouraged to communicate his observations to headquarters. Nowhere could these communications be more sure of a kindly and sympathetic reception than at the hands of the Hydrographer. He used to write appreciative letters to the authors of them, and where the observations seemed to be of sufficient novelty and importance he spared no pains to have them published either by the Admiralty or in the pages of some scientific journal.

In 1886 Captain Wharton was elected a Fellow of the Royal Society,

serving on its Council from 1888 to 1889, again from 1895 to 1897, and lastly from 1904 until his death.

As a Fellow of the Royal Astronomical Society, as well as of the Royal Geographical Society, of which he was Vice-President, and as member of numerous committees, he rendered services only less important than his official work at the Admiralty. His first contribution to the publications of the Royal Society was the investigation of the great waves produced by the eruptions of Krakatoa in 1882, which had been begun by the late Sir Frederick Evans and left unfinished at his death. In 1893 he edited the journal of Captain Cook during his first voyage round the world. At the meeting of the British Association at Oxford in 1894, he presided over Section E. Many contributions to 'Nature' appeared from time to time from his pen, the investigation of the origin and formation of coral reefs being a subject of especial interest to him. On this question he advanced a theory, based upon the result of the surveys of a large number of these reefs, that the effect of wave action was mainly accountable for the striking uniformity of depth so frequently met with over the interior of coral banks in the open ocean. He insisted that the erosive influence of the waves in open oceans extends to greater depths than had previously been considered possible.

As a member of the Coral Reef Committee of the Royal Society, he was largely responsible for the selection of Funafuti as the atoll to be investigated by sounding and boring operations, and he was instrumental in securing the co-operation of the Admiralty in the work, which has produced such valuable results in the monograph published by the Royal Society. He was keenly interested in the project for Antarctic exploration, but more particularly in its bearing upon terrestrial magnetism, and he took an active part as a member of the Joint Committee of the Royal and Royal Geographical Societies appointed to organise it.

He was placed on the retired list in 1891, in accordance with the regulation respecting non-service at sea. Promoted to Rear-Admiral on January 1, 1895, on the Queen's birthday that year he was nominated as C.B. On the occasion of the Diamond Jubilee in 1897 he was created K.C.B.

On July 31, 1904, Sir William Wharton resigned the office of Hydrographer. For some years previously he had suffered much inconvenience and pain owing to an injury to his right wrist received whilst serving in the "Shearwater"; for this and other causes he determined to relinquish the appointment. In July, 1905, after a visit to Aix-les-Bains, he accepted with some hesitation the reiterated invitation to go out to South Africa with a party of members of the British Association, and he presided over Section E at Cape Town. Unfortunately he fell ill on the return journey from the Victoria Falls, and could not return to England, as he intended, with his friends. His illness, which was at first thought to be a chill, proved to be enteric fever complicated with pneumonia, and although no effort was spared to effect his recovery he died at the Observatory at Cape

Town on September 29, where he was the guest of his old and valued friends Sir David and Lady Gill. He was buried at the Naval Cemetery at Simon's Town on October 1, with naval honours, H.M. the King being represented by the Commander-in-Chief of the station. He was married in 1880, to Lucy Georgina, daughter of Mr. Edward Holland, of Dumbledon, in Gloucestershire, and by her, who survives him, he had two daughters and three sons, two of whom are now serving in H.M. Navy.

A. M. F.

SIR CHARLES WILLIAM WILSON. 1836—1905.

CHARLES WILLIAM WILSON, second son of Edward Wilson, Esq., J.P., of Hean Castle, Pembrokeshire, was born in Liverpool, March 14, 1836. He received his education, first at St. Davids, and later at the Liverpool Collegiate Institution, at Cheltenham College, and the University of Bonn. In his nineteenth year he entered the Royal Engineers, gaining second place in the open competition and was gazetted Second Lieutenant, September 24, 1855.

His special fitness for pioneer work was early recognised, and in 1858 he was selected to serve as Secretary and Superintendent of transport and commissariat arrangements to the Commission for the Survey of the boundary between Canada and the United States. By the Treaty of 1846, the parallel of 49° N. had been constituted as the boundary line, but the earlier surveys made from the Atlantic coast had only been carried as far west as the meridian of 95° W., ending at the Lake of the Woods, close to the western extremity of the Province of Ontario. The survey party of 1858, under the command of Colonel Hawkins, the Chief Commissioner, began their operations at Boundary Bay, on the Strait of Georgia, and worked eastward through the difficult and uncivilised region of swamps, forest, and mountain, as far as the meridian of 114°, ending at the eastern boundary of British Columbia, on the eastern range of the Rocky Mountains. In the latter part of the work much of the superintendence of the actual survey was committed to Lieutenant Wilson, and on the completion of the survey in 1863 he received the thanks of the Secretary of State for Foreign Affairs, and was promoted to the rank of Second Captain.

In August, 1864, Captain Wilson undertook the task of making a survey of Jerusalem and the surrounding country, in connection with the scheme originated by Miss Burdett Coutts for providing a supply of pure water to that city. This work he accomplished with signal success, and he carried his survey through the country to the east of Jerusalem, as far as the Dead Sea, of which he determined the level. Owing to local intrigues, the project of the water-supply was not then proceeded with, but the maps and plans made by

him are of permanent value and have been the groundwork of all subsequent topographical research in this region. He published descriptive notes explanatory of his maps at the time, and at a later date he wrote a short paper on the water-supply of Jerusalem.

The interest aroused by the researches of Captain Wilson, as well as his direct personal influence, led to the organisation, in 1865, of the Palestine Exploration Fund, and the Executive Committee of that body appointed him as the first Director of the Exploration. In this capacity he returned to Palestine in 1865, and made a preliminary survey of a large part both of Judæa and Galilee. He made plans and drawings of many ancient sites and ruins, and carried a line of Azimuths from Banias to Jerusalem. From this work he was recalled to take part in the Ordnance Survey of Scotland in 1866, and was succeeded by Captain (now Sir Charles) Warren. In recognition of the value of his survey he was elected member of the Executive Committee of the Palestine Exploration Fund, and later he was awarded the Diploma of the International Geographical Congress at Antwerp, in 1871. While connected with the Scottish Survey he acted as Assistant Commissioner on the Borough Boundaries Commission in 1867.

In 1868 he again visited the East to make, in conjunction with Captain Palmer, a survey of the Sinaitic peninsula, a difficult task which he accomplished in less than six months. His notes of this exploration were published in the following year. On his return he was appointed Executive Officer in the Topographical Department of the War Office, and in 1871, on the expansion of this branch into the Intelligence Department, he became its Director, with the rank of Assistant Quartermaster General. He was in this year elected Member of Council of the Royal Geographical and of the Biblical Archæology Societies, and in 1872 received the decoration of C.B. (Civil). In the following year he was promoted Major of Royal Engineers.

He was elected a Fellow of the Royal Society in 1874, and in that year was President of the Section of Geography of the British Association.

The next task entrusted to him was the compilation of the map of Afghanistan for the India Office. For this work, which he completed in 1875, he received the thanks of the Secretary of State for India. In the following year he was appointed to the Command of the Ordnance Survey of Ireland, in succession to Lieutenant-Colonel Wilkinson, and held that office until 1879. During his tenure of this office he also served on the Royal Commission for the Registration of Deeds and Insurances, and while in residence at Mountjoy Barracks he was a frequent and welcome guest at the Council breakfasts of the Royal Zoological Society, and took much interest in the work of that Society.

In 1878 he was again ordered abroad to serve as British Commissioner for the delimitation of the boundaries of Servia under the Treaty of Berlin. For his services in that capacity he received the thanks of the Government, and was promoted Brevet Lieutenant-Colonel in 1879.

On account of his remarkable knowledge of Eastern affairs he was

appointed in 1879 to the responsible post of Consul-General in Anatolia. While he held this office he travelled through little-known parts of Asia Minor, and was sent on special missions to Bulgaria, Macedonia, and Roumelia. Much of the information which he thus collected is embodied in the "Handbook to Asia Minor" and the "Handbook to Constantinople," edited by him for Murray's Series. For these services to the Foreign Office he was accorded special thanks, and he received the Order K.C.M.G. in 1881. In that year he was also promoted Regimental Lieutenant-Colonel.

On the outbreak of the rebellion of Arabi Pasha in 1882 he accompanied the force under Sir Garnet Wolseley to Egypt, and took his share in active military service. On the suppression of the insurrection he served under Sir Edward Malet, and was put in charge of several important matters; among others he was appointed to superintend the prisons in which the political prisoners were confined, and to watch their trial, on behalf of the British Government. In the discharge of these duties there were many difficulties to be overcome, but these he surmounted with much tact and discretion, and received the thanks of the Government and the rank of Brevet-Colonel in 1883.

When Lord Dufferin's Commission was sent for the reorganisation of the Egyptian Administration, Colonel Wilson was appointed on the Staff, and in this capacity his attention was directed to the affairs of the Soudan, where the Mahdi Mohammed Ahmed had proclaimed himself as the prophet foretold by Mohammed and had raised the standard of rebellion against the Egyptian Government in August, 1881. On this subject Colonel Wilson made a report in 1882 to the Consul-General, and recommended that a British force should be sent to Khartoum to examine and report on the steps which were required for the quieting of the native unrest. In accordance with the suggestion in this report, Colonel Stewart was sent thither and made his report in 1883, but the recommendations made therein were shelved, although by that time the rebellion had become a formidable menace to Egypt after the crushing defeat of Assuf Pasha. Meantime Sir Charles Wilson was recalled home to his former post as Director of the Irish Ordnance Survey. The British Government imperfectly realised the gravity of the situation, and sent, in 1884, General Gordon for the purpose of withdrawing the isolated garrisons of Egyptian troops from the Soudan. The subsequent events are matters of history, and need not here be detailed. When the Government realised the necessity of sending an expedition for the relief of Gordon, Sir C. Wilson was appointed Chief of the Intelligence Department with Lord Wolseley's force, and joined the Army in September, 1884, with the rank of Deputy Adjutant and Quartermaster-General. The expedition reached Korti, south-east of Dongola, on December 16, 1884, and on January 8 Sir Herbert Stewart and Sir Charles Wilson were sent on with the Camel Corps to communicate with Gordon, and to let him know that a relief expedition was on the way. The instructions were explicit that Wilson was only to stay long enough to confer with General Gordon and to return

then at once with Lord Charles Beresford to Matammeh. In his book on the expedition "From Korti to Khartum" (1886), Sir Charles Wilson has given a graphic account of this disastrous journey and of the chapter of accidents which delayed it. As Sir Herbert Stewart was wounded at Abu Klea the command devolved upon Sir Charles Wilson, and he started from Gubat at the earliest possible opportunity, on the 24th January, for his four days' journey up the Nile, only to learn that Gordon had been killed on the 26th. Even had he arrived two days earlier with the small and undisciplined force under his command, he would have been unable to alter the course of events, and would most probably have shared Gordon's fate.

For his services in this expedition he received from the Secretary for War a telegram of "warm recognition of Government of brilliant services of Sir Charles Wilson, and satisfaction at gallant rescue of his party." He was specially mentioned in Lord Wolseley's despatches, and was created K.C.B. in 1885.

Shortly after his return home he was appointed Director-General of the Ordnance Survey, and began the revision of the Irish Survey maps on the 1/2500 scale, as well as the Survey of Yorkshire and Lancashire on the same scale. He also carried on a general revision of the small scale maps, so as to bring them up to date. He initiated a scheme for the organisation of Survey sections for service with an army in the field. He continued in command of the Survey until 1894, having been promoted Major-General on February 15 in that year. In the next year he was appointed Director-General of Military Education, an office which he held until 1898, when he retired under the age clause of the Royal Warrant. While discharging these duties he found time to write a "Life of Lord Clive," for the "English Men of Action" series published in 1890. Sir Charles Wilson served on the Council of the Royal Society, 1889–90, and his work was recognised by the conferring on him by Oxford of the honorary degree of D.C.L. in 1883, by Edinburgh of the degree of LL.D. in 1886, and by Dublin of the degree M.E. in 1893.

Through all the stages of his varied career he kept up his interest in the work of the Palestine Exploration Fund, and on the retirement of Mr. Glaisher he was unanimously elected Chairman of its Executive Committee. The duties of this office he discharged with unremitting zeal, keeping himself in touch with the progress of the work of exploration in the field, visiting the excavations both at Tell Zâkariyeh and later at Gezer. For the last year of his life his work was hindered by a severe affection of the eyes, but he continued to edit the "Quarterly Statement" of the Fund and to attend its committee meetings almost to the end. The last research on which he was engaged was an exhaustive study of the evidence as to the site of the Holy Sepulchre, and he had almost finished the revision of his manuscript when he was laid aside by his last illness. This book will soon be published by the Palestine Exploration Fund under the supervision of Sir Charles Watson, who has succeeded him as Chairman of the Executive Committee of the Fund. He died on October 25, 1905, at Tunbridge Wells.

Sir Charles Wilson married, in 1867, Olivia, daughter of Colonel Adam Duffin, Bengal Cavalry, who survives him; he also leaves a daughter and four sons, three of whom are officers in the Army.

He was in manner quiet, courteous, dignified, and remarkably unobtrusive, but one could not be long in his company without realising his quick and correct judgment of men and affairs, his wisdom and firmness of purpose, his kindness and consideration for others, and his extraordinary store of accurate knowledge. Those associated with him on the Committee of the Palestine Fund learned to rely implicitly on his advice, and willingly to accept his decisions as final. They feel that they have lost a wise and judicious friend indeed, and have stated in their last published report that his death is "the severest personal loss that the Fund has ever sustained."

In addition to the published works referred to, Sir Charles Wilson was also the author of: 1. "The Recovery of Jerusalem," 1871. 2. "Jerusalem the Holy City," 1889. 3. "Picturesque Palestine, Sinai and Egypt," 4 vols. 1880. 4. "The Pilgrimage of the Russian Abbot, Daniel," 1895.

The writer is deeply indebted to Sir Charles Watson for much of the information embodied in this biographical notice.

A. M.

OTTO STRUVE. 1819—1905.

THE death of Otto Struve on April 14, 1905, closes more than one chapter in the history of Astronomy. One such chapter might be headed "The Pulkowa Observatory," and we should find Otto Struve's name on almost every page from the first to the last. At the foundation of the Observatory in 1839, he went as assistant to his famous father; within a very few years he began to perform some of the Director's duties, and long before he officially succeeded his father in 1864 he had been practically the head of the Observatory. When at last he left Pulkowa after 50 years spent in its service, the "Pulkowa Observatory" officially ceased to exist* and became the "Observatoire Central Nicolas."

Changing our historical arrangement a little, and classifying by lines of investigation rather than by localities, there is a great chapter on "Double Stars" written by the two Struves, following that written by the Herschels. Otto's name does not occur here till nearly the middle of the chapter; unless perhaps we find room on the first page, when mentioning the publication of W. Struve's first Catalogue of 727 stars in 1820, to record the recent birth of the son who was to be so worthy an assistant and successor.

Once again, regarding not the doings of a single observatory or the history of one branch of astronomy, but taking a more general outlook on the spirit of the times, we realize that in Otto Struve there passed away a commanding figure of the "old school" of astronomers. An attempt to define too closely the characteristics of this school would inevitably result in error and failure: but it is significant that the fourteen volumes of observations published under Otto Struve's Directorate all relate to the *positions* of stars, and contain no allusion to the spectroscope or the photographic plate. Nevertheless (and there could not be a better illustration of the dangers of being too definite) we must at the same time remember that the very existence of the department of Astrophysics at Pulkowa is due to him, and that he only established it after considerable trouble. Struve began work at a time when it was scarcely dreamed that Astronomers would ever use the spectroscope or take photographs, and his

* The description of the Observatory published by F. G. W. Struve in 1845 is entitled 'Description de l'observatoire astronomique Central de Poulkova.' Fourteen volumes of observations were published by Otto Struve, entitled 'Observations de Poulkova, publiées par Otto Struve, Directeur de l'observatoire Central Nicolas,' the last words being in quite small type. On Struve's retirement a new series of volumes was started with the style 'Publications de l'observatoire Central Nicolas, Série II.' The last volume of Série I to appear, numbered vol. 10, is dated 1893, and contains Struve's name as "Ancien directeur."

first lessons were calculated to impress indelibly upon his mind the fundamental importance of work in which the spectroscope and the photographic plate have even yet taken no part. His early years were devoted to a determination of the constant of precession, and the value he obtained was adopted for general use. His observations led him to side with Herschel, and against Bessel, on the question (at that time new) whether the Solar system was moving in space. Moreover, he witnessed the determination, about the same time, of the constant of aberration by his father, and of that of nutation by his colleague Peters. He saw the Pulkowa Observatory take a leading place in the astronomical world for its accurate measures of stellar positions, and it was his own life work to help in raising it to that place and maintaining it there. He lived long enough to see a new constant of precession suggested for adoption, after his own had been in use for half a century, and died just as evidence* was being published in support of his old value as against the proposed change.

Otto Wilhelm Struve was born on May 7 (April 25, O.S.), 1819, at Dorpat, where his father was Professor in the University and Director of the Observatory. He was the third in a family of 18 children. He completed his gymnasium and university course early and was already an assistant to his father when the latter was summoned to found and direct the great Pulkowa Observatory. Otto took his place as assistant in the new Observatory with three colleagues, G. Fuss, G. Sabler, and C. A. F. Peters.

The programme adopted at the outset was the determination of three astronomical constants, aberration by W. Struve, nutation by Peters, and precession by O. Struve; and the success attained has already been mentioned. Other observations of an orderly kind were also carried on, but there was no attempt made to publish them for many years. This fact was lamented by Airy in 1847, and doubtless his representations had some weight in stimulating the ultimate publication of the first two volumes in 1869. But this was after the directorship had passed from the hands of W. Struve into those of his son. It seems proper to recall here, alongside the mention of Airy's action, that we owe to Otto Struve the movement for doing full justice to the observations made by a great Englishman. It was Winnecke, at Struve's instigation, who first undertook the re-reduction of Bradley's observations, though the work passed into the able hands of Dr. Auwers at an early stage.

For the determination of precession, which occupied his early years at Pulkowa, Otto Struve received the Gold Medal of the Royal Astronomical Society in 1850. The work had been completed nine years before, and this fact is apologetically mentioned by the President (Airy) in an interesting manner. "A rather unusual delay," he said, "has occurred in the notice of this paper (on precession). This has arisen partly from the delay which usually occurs in the printing and distribution of foreign memoirs, partly

* 'Mon. Not. R.A.S.,' vol. 45, p. 443. Dated March, 1905, published in April. Struve died April 15.

from the time which is necessary for thoroughly reading a paper of such length; but principally from the occupation of the minds of astronomers, as well within as without the Society, by the remarkable planetary discoveries made in several years past." This was in February, 1850, the discovery of Neptune having been made on September 23, 1846, while six new minor planets had just been found, after a barren interval of 40 years since the first four.

The mention of the discovery of Neptune recalls the fact that Otto Struve was elected an Associate of the Royal Astronomical Society on the same day (May 12, 1848) as Galle, who actually discovered the planet; and Struve's death leaves Galle as the unrivalled *doyen* of the Society, which honoured him a dozen years before any existing Fellow was elected.

But having completed his work on precession, Struve became henceforth a double star observer. We may no doubt trace this bent to his whole-hearted devotion to his father, which is writ large on every page of his published works. It was not in double star observing alone that this devotion found expression. In a memoir of his father left in MS. he has recorded that in 1845 (when he was only 26) he had already practically taken over the duties of administration of the Observatory, though the official acknowledgment of the fact did not follow for many years. Possibly the strain of these early years may have contributed to the serious illness which overtook him in 1864 soon after he was actually appointed Director. The doctors actually gave him up, and though he recovered, he was so broken in health as to think of resignation. A winter in Italy, however, fortunately restored him; and he returned to a long and prosperous term of office and activity. Indeed the length of his record as an actual observer is remarkable; there are certainly one or two measures of double stars recorded as made by him at Dorpat in 1836, and there are others dated 1889. Few indeed can match a record of 53 years as an observer.

But his veneration for his father fortunately did not cramp his originality. He selected for special study stars of a distinctly new type. W. Struve had deliberately chosen double stars with components not differing much in brightness; what first suggested to his son to form a catalogue of stars having faint companions? The difference may at first seem to be one of detail; but it represents an important step taken in the study of double stars, preparing the way for the modern work of Burnham and others.

Another important line struck out by Otto Struve for himself was the investigation of personal peculiarities of measurement. The idea of "personal equation" in a variety of forms is familiar enough to us now; but in 1853 it was only recognized in transit observations, and was deduced from comparison of the observations themselves, not by any attempt at independent determination. Such comparisons of observations *inter se* were, in the case of double star observations, not available in sufficient number to determine personal differences, though there were enough to suggest them. Struve devised his famous artificial adjustable double star to

investigate his own peculiarities. The actual separation and position angle of the artificial double were known; and turning his telescope horizontally towards the distant model and measuring them as he would those of a real double, he found the systematic errors in his measures. The errors were large (13° in position angle in some cases) and were not quite satisfactorily determined with the apparatus, as is intelligible when we remember that the stars in the actual sky are observed with a telescope which is anything but horizontal, and that they are liable to atmospheric disturbances. But Struve obtained at any rate a large measure of success, and was able not only to eliminate the main part of such systematic errors from his future observations, but by comparison to infer suitable corrections for observations already made. The summary of his life-work as an observer is to be found in Volumes IX and X of the Pulkowa Observations, Volume X being completed in 1893.

We must not forget to add the work he did in editing, jointly with Schiaparelli, the two volumes of Dembowski's observations of double stars which appeared in 1883.

It would do scant justice to Otto Struve to regard him merely, or even chiefly, as a double star observer. The range of his interests and activities was very wide. In 1851 he read before the Academy of Sciences an elaborate paper on the Rings of Saturn, suggesting from a discussion of old and recent observations that they were spreading inwards to the planet; (this hypothesis has not been confirmed). Geodetic work absorbed much of his attention, and it was on his initiative that the 47th parallel of latitude, which had been selected for measurement, was given up in favour of the 52nd. By this change the arc was extended at both ends; the eastern end became Arsk in Siberia, and (what is of chief interest to us) at its western end the arc crossed England and terminated in Valencia in the extreme S.W. of Ireland. Recent work on the longitude of Waterville carried out under the direction of the Astronomer Royal has a direct bearing upon the investigation as modified by Otto Struve.

In another enterprise of international interest he was not so successful. He had succeeded in persuading the authorities of the advantages in adopting the Gregorian calendar in general use by other European nations; and the change was under serious consideration in high quarters, when all chance of reform was abruptly destroyed by the dynamite explosion in the Winter Palace.*

On the occasion of the Paris International Conference in 1887, which led to the scheme for charting the heavens by photography, Struve was unanimously called to the chair. His opening address contains a paragraph so characteristic of the man and of the epoch that it may fitly be quoted here.

"En effet, l'Astronomie pratique possède aujourd'hui, dans la Photographie, un instrument de la plus haute valeur et qui, probablement, avec le temps,

* V.J.S. 'Ast. Ges.,' Jahrg. 40, Heft 4, pp. 298–9. To this notice by M. Nyrén the present writer is indebted for much of the information here given.

facilitera énormément nos études épineuses. Mais restons sobres dans nos prévisions. Pour le moment, nous ne devons regarder la Photographie que comme un instrument très précieux, mais dont l'étude reste encore à compléter. Nous devons tâcher d'élever la Photographie céleste à ce degré de perfection qui la rendra digne de concourir sous tous les rapports avec les méthodes d'observation usitées jusqu'à présent, méthodes qui ont valu à l'Astronomie pratique la position enviable d'une science expérimentale dont les conclusions peuvent rivaliser en rigueur avec les théories mathématiques."

These words remind us of those in which Wilhelm Struve opens his description of the Pulkowa Observatory (1845):—"L'Astronomie, par la sublimité de son sujet, occupe une place éminente parmi les sciences naturelles. Elle est, par excellence, la science naturelle exacte."

It may be doubted whether Astronomy in its modern developments will be able to maintain this claim of an exactitude greater than that attainable in other sciences, if indeed it could ever rightly advance it; but there is no doubt that to the Struves the claim was a righteous one, and was the source of no little inspiration.

The Transit of Venus of 1874 brought with it much work of organisation for Otto Struve. So too did the Total Solar Eclipse of 1887. His own preparations for the latter event were characteristically all for observations of position, but some 40 astronomers of other nations visited Russia on the occasion, and Struve made the most hospitable arrangements and careful plans for their comfort. Nearly all of them passed through Pulkowa and were entertained by him at his own house. He took great interest in their proposed work, though much of it was clearly strange to him. For instance, he learned with obvious surprise of the time for preparation required by those desiring to make photographic or physical observations: he had estimated that no one would wish to be at his station more than 2 or 3 days altogether. But on realizing their requirements, he did all he could to secure the requisite facilities. The memory of those few days at Pulkowa, when at the same table, spread in the open air in order to make the most of the short northern summer, there were gathered astronomers from Italy, Spain, France, Germany, America, and England, to each of whom Otto Struve spoke in his own language; when we caught a glimpse of the daily life of the little secluded community, with such special features as the disappearance of all the males in the afternoon to sleep, so that they might be regularly on the alert for observations till 3 A.M.; when we were privileged at night to look through the great 30-inch refractor, which had not then been thrown into shade by the Lick and Yerkes telescopes;—the memory of these days will long remain with astronomers of many nations. They were almost the last days of Struve's life at the Observatory. Two years later, in 1889, there was again a great gathering of foreign astronomers to celebrate the Jubilee of the foundation of the Observatory: but Struve's resignation had already been accepted, although it had been decided, by the

express wish of the Czar, that he should remain in office until the ceremony was completed.

Otto Struve was twice married: first to Emilie Dyrssen, who died in 1868; secondly, to Emma Jankowsky, who died in 1902. He celebrated the "silver-wedding" of both marriages. By his first wife he had several children, of whom 4 sons and 2 daughters reached maturity, though one died before her father; by the second wife he had one daughter. Of the sons the two youngest are well known astronomers: Hermann, Director of the Berlin Observatory, who received (in the third generation) the Gold Medal of the Royal Astronomical Society in 1903 for his brilliant work on the satellites of Saturn with the great Pulkowa refractors; and Ludwig, Director of the Charkow Observatory, who followed in his father's footsteps by determining the constant of precession and the movement of the solar system.

The honours conferred on Otto Struve would make a long list, for he was a foreign or corresponding member of almost all European learned societies. The date of his recognition by the Royal Society is 1873. In 1868 the Bonn University conferred a Doctorate upon him, *honoris causa*.

After his retirement from Pulkowa he lived a few years in St. Petersburg; later in Karlsruhe, on account of failing health; though until recently he paid a visit to St. Petersburg every summer. He died without any serious protracted illness, in his 86th year, on April 14, 1905. By his own wish his ashes are to be taken to Pulkowa and laid under the stone on which his own special instrument, the 15-inch refractor, stood at the time of his observations.

H. H. T.

GEORGE JAMES SNELUS, 1837—1906.

THE subject of this notice was born at Camden Town on June 25, 1837. He was originally trained as a teacher at St. John's College, Battersea, and subsequently, while following this profession, he attended lectures at Owens College, Manchester. It was here, under Professor Roscoe, that Mr. Snelus laid the foundation of his success by his study of Chemistry and Metallurgy. In 1864 he gained the first Royal Albert Scholarship, and consequently entered upon a three years' course at the Royal School of Mines. Here he succeeded in obtaining the Associateship in Metallurgy and Mining, and was awarded the De la Beche medal for mining. At the end of his course he was recommended by Dr. Percy for the post of chemist at Dowlais Works, and he remained there until 1871. In 1869 he was elected a Member of the Iron and Steel Institute, and the brilliant series of papers, representing a large amount of true pioneering work, read before that body in the early seventies will secure for him a lasting place in the annals of the iron and steel trade. He was elected a Member of the Council in 1881, and during the next twenty-five years no one attended the meetings more regularly or took a greater interest in the general development of that body. He became a Vice-President in 1889. In 1871 Mr. Snelus was selected by the Iron and Steel Institute to visit the United States, and report on the chemistry of the Dank's rotary puddling process, and the report, when completed, proved to be the most important contribution ever published on the scientific features of the puddling process.

Whilst at Dowlais Mr. Snelus made observations which led him to the conclusion that phosphorus could be removed from iron while the metal was in the molten state. Experiments showed him that lime could be burned at a high temperature so as to be impervious to water, and it occurred to him that if he used lime so over-burnt as a lining for a Bessemer converter he would get a basic lining which would not be acted upon by basic slag, and so would be able to eliminate the phosphorus during the Bessemer process. He took out a patent for this in 1872, and soon afterwards proved experimentally the correctness of his surmise. The invention, however, was not pushed forward or made a practical success in his hands, and it was not until the "basic process" had been developed by Messrs. Thomas and Gilchrist, with the assistance of Mr. E. P. Martin, Mr. E. W. Richards and his metallurgical staff, that it came into commercial operation. It is an undisputed fact that Mr. Snelus was the first to make steel in a lime-lined Bessemer converter.

For his invention in connection with the basic steel process Mr. Snelus was awarded a gold medal at the Paris Exhibition of 1878, and in 1883 the Iron and Steel Institute recognised the part he had played in developing the process by awarding him, jointly with Mr. Thomas, the Bessemer medal.

For his discovery, and for his numerous and valuable literary contributions connected with iron and steel, Mr. Snelus was made a Fellow of the Royal Society in 1887. During the period 1869—1885 he wrote and spoke on a great variety of matters connected with the manufacture of iron and steel, and he was really the first to bring to the notice of iron and steel works' chemists in this country the true practical value of the molybdate method of determining phosphorus in iron and steel. Indeed, it was mainly due to the influence of Mr. Snelus that chemists in steel works learnt to make analyses sufficiently rapidly to be of value in controlling the manufacture of steel.

He went to Cumberland in 1872 and took up the position of manager of the West Cumberland Iron and Steel Company, where he remained many years. Subsequently these works were discontinued and to a large extent dismantled. From that time Mr. Snelus did not undertake managerial work, although he was director of several companies engaged in the iron trade.

Only quite recently he had invented a new process for the manufacture of steel, by which a basic-lined rotary furnace is employed. Whether this new process will prove a success remains to be seen.

Much of his leisure time was devoted to Volunteering and rifle shooting. He served as a Volunteer for 32 years, and was, for many years, one of the best rifle shots in the country. He was for twelve years from 1866 a member of the English Twenty, and during that period gained a greater aggregate than any other member of the team. Mr. Snelus was also an enthusiastic horticulturalist and a staunch Conservative, and was keenly interested in local affairs, public bodies seeking eagerly for his services.

He married Miss L. W. Woodward, daughter of Mr. David Woodward, of Macclesfield, and had three sons and three daughters. Mrs. Snelus died in 1892. Mr. Snelus spent a busy life until his health broke down. After a long illness he died at Ennerdale Hall on June 18, 1906.

J. E. S.

CHARLES JASPER JOLY, 1864—1906.

CHARLES JASPER JOLY was born in Tullamore, Ireland, on June 27, 1864. His father, the Rev. John Swift Joly, was a man of studious bent and author of archæological studies of local interest. It can hardly be said that any of the more nearly antecedent ancestors of Charles Jasper foreshadowed his remarkable gifts. The family is French on the father's side, having emigrated from France so long ago as the middle of the eighteenth century. If heredity is to be appealed to for Joly's mental powers, it is necessary to go back to the seventeenth century, when Claude Joly, an author of distinction, appeared among his ancestors, but not in the direct line. The family claims, however, direct descent from Jacques Joly, a Secretary of State (about 1640), and from Reginald, born 1375, who was "Conseiller" in 1420, as well as from Antoine Joly, of Blaisy-en-haut, a seigneurie in Burgundy, near Dijon, which was erected into a Marquisate in favour of the said Antoine.

Charles Jasper was a brilliant boy at Galway Grammar School, appearing able, when so inclined, to win whatever medals and prizes he aspired to, and even several at one time. In the public Intermediate Examinations he took prizes and honours, but although possessed of this amount of reputation when he entered Trinity College, Dublin, in his eighteenth year, the exceptional powers which he subsequently developed were not indicated in his school career. Even as a student in Trinity College there was nothing accomplished by Joly that has not been accomplished by many a man who subsequently remained without further distinctions through life. He took a mathematical scholarship—by no means on specially brilliant marks—and finally won a mathematical studentship, but, again, without the distinction of the "Large" gold medal. His second subject at this examination was Experimental Science.

After leaving Trinity College he went to Berlin and entered Helmholtz's Laboratory with the intention of making Experimental Physics his life study. There he worked under Koenig's supervision, and would, doubtless, have carried out his intention of giving himself up entirely to the fascination of Physical Research had not the death of his father recalled him to Ireland and rendered it necessary that he should seek some more sure road to a competency. That he altered his intention of devoting himself to Experimental Science was perhaps for the best. For, while he certainly never showed any exceptional originality in that direction, his after career fully justified his diversion to mathematics.

The possibility of attaining to the Fellowship of his own College induced him to pursue the mathematical and mathematical-physics courses required for the mathematical side of this test. The severity of this competition is

intensified by the extraordinary arrangement permitting candidates in mathematics and classics to compete against each other; the successful candidate being the winner of highest marks, where subjects, papers, examiners are different. For this ordeal it is not uncommon for men to read for five or seven years; not, perhaps, acquiring fresh wisdom after the first two or three years' reading, though gradually becoming more proficient in the art of scoring.

Year after year Joly fell short of success. Year after year he read Dante and other masters of literature, and, led away by the facile charms of literary studies, he plunged, forgetful of everything else, into the real or unreal world of poetry and romance. It was at this period that my own more intimate friendship with him commenced. Besides the tie of relationship, we had many tastes in common. In the course of our endless discussions and speculations there was revealed to me a mind both keen, critical, and honest; a nature undemonstrative, sincere, and deeply affectionate.

It was not till 1894 that Joly was successful in his efforts to gain Fellowship. He appears to have attained something more than Scholarship by the long and arduous preparation required for this trying test. He was injured neither in freshness of originality nor in bodily health. He set to work almost immediately he became Fellow on mathematical work, the only holiday intervening being the annual Swiss tour.

A word must be said here on Joly as member of the Alpine Club. His development as mountaineer was as unexpected as his mental evolution. Delicate in appearance, pale in complexion and with rather stooped shoulders, no one would have predicted the athletic prowess he displayed. But two factors were in his favour: he possessed undaunted courage and a power of endurance which must have had its origin also in a marvellous nervous organisation. A very few years later I was with him in circumstances of considerable danger, when on the arête of the Eiger we made our way downwards in the midst of a furious snow storm. Joly led the way with a skill and nonchalance which even in the midst of our troubles claimed our attention. Later, climbing became a passion with him, and his holidays were passed in the Alps, ascending the most difficult peaks. The Dent Blanche, Kleine Zinne, and many others were ascended. (See notice by Dr. George Scriven, 'Journal of the Alpine Club,' February, 1906, vol. 23, p. 58.)

The first work to appear from his pen, "The Theory of Vector Functions," was read before the Royal Irish Academy in the same year in which he got his Fellowship. A second paper on the subject of Vector Linear Functions appeared in the ensuing year, 1895, and two others the next year.

At this period his marriage with Jessie, daughter of the late Robert Meade, took place.

Later in the year 1897 the Board of Trinity College appointed him to the Andrews Professorship of Astronomy and to the post of Royal Astronomer of Ireland. The appointment was a particularly happy one, although at the

time there was some difference of opinion as to his suitability for the office. But not only had Joly considerable training in manipulative scientific work, he was already recognised as highly accomplished in the Mathematics of Hamilton, and possessed of originality and activity. All through his reading for the Fellowship he had been more and more drawn to the use of Sir William Rowan Hamilton's mathematical methods, and it was even stated at the time that his examiners had themselves some difficulty in following the young mathematician in his facile use of Quaternions.

The election accomplished, Joly took up his abode in the historic house of Dunsink, wherein Brinkley, Hamilton, and Ball had done much of their best work. Joly now had the freedom from the too constant invasion of visitors and friends and the quiet and healthful surroundings favourable to mental activity. Never, indeed, had the life of a recluse any charm for him. He associated himself with some of the most important Institutions of the City of Dublin and never failed the committee which had a claim upon him. But he was spared petty interruptions. His teaching duties as Professor of Astronomy were light—one Term in the Session—and an able and careful Assistant was at hand to do the bulk of observational work. The mornings were generally free from disturbance, and, as will be seen, an amazing amount of work was done during the next few years of this quiet life.

Many who read this brief memoir will know the beautiful precincts in which Joly and his predecessors have done such good work. The old House commands from the south windows an extensive view. The panorama of the Dublin Hills—the rounded granite hills of Leinster—rising one beyond the other, invite the imagination into the furthest distance. Between lies a broad and noble valley containing in the near distance the lawns and woods of Phœnix Park, and to the east the City of Dublin. The pastoral element predominates, however, and, seen from this view-point, Dublin might appear to be a city girt with peaceful lawns and forest trees. Further yet, beyond the "towers, domes, citadels," the Bay of Dublin stretches to the horizon. A more varied sweep of mountains, forest, city and sea it would be hard to find. From the south window of the study an observer lifting his eyes can, at a glance, review it all. Around the house is the fruit garden and shrubbery, planted by Brinkley and Ball, and the old-fashioned box-trimmed flower garden merging into the orchard. Tall trees line the shady walk leading to the gate in the wall where suddenly is revealed to you, across steeply sloping fields, the same majestic panorama of mountains and woods seen from the study window.

In this home Joly lived to the end of his brief life, its quietness and its beauty contributing to his work and to his happiness.

A period of ever-increasing mental activity followed upon his appointment. The great work of editing 'Hamilton's Elements of Quaternions' and bringing this vast treatise up to date was already upon his hands. It had now to be completed, but its completion did not hinder Joly from continuing the publication of papers on various mathematical subjects. Thus we have a

paper on "The Associative Algebra Applicable to Hyper-space" in 1897; one on the Congruency of Curves in 1899; and still others in 1900 and 1901. In 1900 he accompanied the Eclipse Expedition sent out by the Royal Dublin Society and the Royal Irish Academy, to Spain, and obtained some exquisite photographs of totality.

In 1899 the first volume and in 1901 the second volume of the new edition of Hamilton's Elements appeared. What the editorial work involved in patient and brilliant scholarship will only be appreciated by those acquainted with the vast and difficult literature which had to be analysed and embodied in the new edition. About 150 quarto pages of new matter were added.

During the couple of years succeeding this editorial work Joly was mainly occupied in extending his reading in Astronomical Science. Two other papers on mathematical subjects, however, appeared during this interval, and the laborious work of editing a new edition of Preston's 'Treatise on Light' was accomplished.

In December, 1902, Joly's paper on "Quaternions and Projective Geometry" was communicated to the Royal Society by Sir Robert Ball and appeared in the 'Transactions.' We ourselves know that the writer regarded this as a great advance and as a hopeful extension of the utility of Quaternions to new fields of investigation. His name was put up for Fellowship in the Royal Society in 1904 and his election followed the same year.

In the year 1905 the Manual of Quaternions appeared. I have omitted reference to various mathematical papers which preceded this work. The Manual appeared in the centenary year of Hamilton's birth. The work was written in a marvellously short space of time—about a twelvemonth. He however, wrote mathematics, worked out examples, and pursued his reasoning with the facility and ease with which a ready writer of fiction might develop the events of a novel. This, about his last great work, was received with commendation on every side; a reception all the more flattering as those who were admirers of Tait's treatment of the subject had to adapt themselves to a somewhat different mode of development before they could appreciate the new writer's work. Indeed, the Hamiltonian method of establishing the laws of Quaternions is here in part abandoned. In this work the author makes use of a wonderfully extensive knowledge of the mathematics of every branch of Physical Science.

In 1905 he took part in the visit of the British Association to South Africa. It was shortly after his return that first his little daughter and then he himself contracted the illness (typhoid) which, after a protracted period of many weeks, during which his strength was slowly sapped, gave rise to a complication (pleurisy) against which he could no longer contend. To the last moment of consciousness he showed the same unselfish consideration for others which was one of his most lovable characteristics. At a little after midnight—early on January 4, 1906—he passed away unconsciously.

In the last year of his life he acted as secretary to a Committee appointed by the Board of Trinity College to enquire into the mode of election to

Fellowship in Trinity College. A serious constitutional evil is undoubtedly existent in the exclusively examinational nature of this mode of selection. Joly never mentioned this matter without disapproval, and the Committee was appointed largely at his request. He gave much time and thought to its work, but the recommendations of the Committee led to no remedial measures. The appointment of a Government Commission, to which he had often looked forward as probably the only hope of drastic reform of this and other constitutional evils, took place a very few months after his death. It would be hard to estimate how much of the time and thought of distinguished Trinity men have been absorbed upon this hitherto fruitless subject of contemplation. It must be remembered that the constitution of their University regulated the lives and surroundings of these men. Every feeling of loyalty to their University as well as every disinterested desire to benefit the higher education of their country, acted to urge into action men of the stamp of FitzGerald and Joly.

His extraordinary powers of mathematical head-work are known to his more intimate associates. The problem stated, Joly's blue eyes sparkled with an expression which might more readily be taken for mirth than for abstraction. A characteristic gesticulation in these moments of thought was the stroking of his short beard. In an astonishingly short time the solution often came—perhaps more than one—and not till then was pen and paper resorted to that the enquirer might have it put before him. Men of very considerable mathematical training who had sought in vain for the solution and got it in this way were naturally impressed. There was undoubtedly a comprehensiveness in his learning which has rarely been excelled even by the greatest of mathematicians, and it must be remembered that almost his entire work was accomplished within the short space of 10 years; far the greater part within the last five years of his life. This rapidity of production indicated both thoroughness of knowledge and swiftness and sureness of reasoning. The remarkable powers of head-work were but the expression of these accomplishments and gifts. He possessed, in common with FitzGerald, a wonderful power of abstraction from immediate surroundings. Much of his work was done while conversation was going on around him. Joly generally reclined on a sofa when writing. The paper was held on his knee. The actual work was done in this attitude. A final copy was then typed.

He wrote a clear and simple style of English, without effort or affectation. Most of his letters might be sent to press without a word of alteration. Full of point, too, are they, and of clever criticism. Much of his correspondence with Sir Robert Ball will be preserved in the Library of Trinity College, Dublin. It largely refers to the Theory of Screws.

It is beyond my powers to convey the impression which Charles Joly made upon me. His books and papers speak for his rare gifts; and his best and most esteemed friend—among many friends—adds to this short notice an estimate of his mathematical work.

The circumstances of Joly's early death are indescribably sad. He was

literally only beginning when life closed for him. A future excelling all his past was assured to him had the toil of youth but met its just reward and the harvest of life been his. The happy domestic life, the rare and precious gifts—honours of life so meekly borne—the whole bright future, all to be laid aside!

When he knew he was attacked by the dangerous illness which ended all, he wrote to a friend: "If the attack is as severe as Jessie's (his little daughter), I know quite well I cannot hold out. For myself I am content, though I should have given much to save the pain that others may feel. I confess also that I should like to be allowed to finish my life's work. Many unsolved problems might have some light thrown upon them if I had a little more time. I might have a useful influence in the affairs of College. I feel it would be a pity"—.

At the time of his death his hands were full of work. He had undertaken the article on "Quaternions" in the new edition of the 'Encyclopædia Britannica,' and had already entered upon the formidable duties of editing the whole of the articles on "Optics" for the same work. An unfinished Elementary Astronomy, having many features of novelty of development, remains behind, as well as a nearly finished Treatise on Solid Geometry. The latter promises to rank among his best writings.

Joly was, at the date of his death, Secretary of the Royal Irish Academy, Trustee of the National Library of Ireland, Member of Council of the Royal Dublin Society, and President of the International Association for Promoting the Study of Quaternions and Allied Systems of Mathematics.

J. J.

Professor Joly's paper on the "Theory of Linear Vector Functions" (1895), T.R.I.A., vol. 30, p. 597, was the commencement of a remarkable series of Memoirs on Quaternions, which has largely extended the applications of Hamilton's splendid invention. At the close of this paper he gives for the first time the relation between the theory of linear vector functions and the theory of screws.

In 1899 the first volume of the Second Edition of "Hamilton's Elements of Quaternions" appeared under the Editorship of Joly, and in 1901 this was followed by the second volume. The important work thus done in rendering Hamilton's masterpiece accessible has been greatly enhanced by the numerous notes and copious appendices which Joly has himself supplied. Attention may also be given to the significant words in the Preface in which Joly says: "My task as Editor has convinced me of the extreme caution with which any endeavour should be made to improve or modify the calculus of Quaternions." Joly, following to some extent the example of Tait, has made very extensive use of the linear vector functions. This beautiful part of the theory is shown to be admirably adapted to many different classes of physical investigation. In a remarkable appendix, Joly also shows how Quaternions provide the most natural method of investigating

the systems of rays, which formed the subject of a famous Memoir of Hamilton in his early days and long before the Quaternions were thought of. Perhaps the part of the appendix which will be most generally appreciated is that on the operator Δ, of which many applications to hydrodynamical and other problems are given.

On the conclusion of this great work Joly turned his attention to the further development of Quaternions by continuing his original Memoirs. Such was his industry and so fertile was the method of Quaternions in his hands that in 1902 three important Memoirs appeared. The first contained an entirely novel development in which a Quaternion is represented as a point symbol. The point is supposed to have a weight equal to the Scalar of the Quaternion, while the vector of the point from a fixed origin is the quotient of the vector of the Quaternion by the Scalar. This was followed by another Memoir in which screws were represented as weighted points, and also by another on Quaternion arrays.

The year 1903 was one of still greater activity. An important paper appeared in the 'Phil. Trans.' (vol. 201, pp. 223—327) on "Quaternions and Projective Geometry." In this is developed the theory of the linear Quaternion function depending upon a latent biquadratic as the linear vector function depends on a latent cubic. The investigation exhibits the relation of Quaternions to Projective Geometry in quite a new light. Another Memoir in this year is on the Quadratic Screw System, in which a very large theory is most ably set forth. It was followed by a shorter Memoir on the Geometry of a New System of Screws. Here, again, the theory of linear vector functions is employed with much effect to set forth geometrical problems.

But, doubtless, the most important work in Quaternions with which the name of Joly will be remembered is his "Manual of Quaternions" which appeared in 1905. In this volume he follows at the outset a slightly different procedure from that adopted by Hamilton. Joly makes the result of the product of two vectors a matter of definition. There seems to be much gain from the point of view of the student in this modification. But the student, while he appreciates the facilities thus given at the beginning of his acquaintance with a new subject, will, as he advances, find it advantageous to turn to Hamilton and read his beautiful reasonings on the interpretation to be given to a product of two vectors.

By the excursions which Joly takes into various departments of Mathematical Physics such as the theory of Strain, Spherical Harmonics, Hydrodynamics and Electro-magnetism, the student of the Manual of Quarternions is introduced to regions far beyond those discussed by Hamilton, though not perhaps beyond those to which he foresaw his calculus might be extended. Indeed, the present state of Quaternions, to the advancement of which Joly has so largely contributed, goes far to justify the aspirations of Hamilton himself. Writing fifty years ago to Humphrey Lloyd, afterwards Provost of Trinity College, Dublin, Hamilton, says :—

"In general, although in one sense I hope that I am actually growing modest about the Quaternions, from my seeing so many peeps and vistas into future expansions of their principles, I still must assert that this discovery appears to me to be as important for the middle of the nineteenth century as the discovery of fluxions was for the close of the seventeenth."

R. S. B.

NOTE.

Obituary Notices of the following deceased Fellows are in preparation for press, to appear in the B Series of the 'Proceedings':—

Sir John Burdon Sanderson, Bart.
Henry B. Medlicott.
William T. Blanford.
Professor Thomas G. B. Howes.
Baron Ferdinand von Richthofen.
Captain Frederick W. Hutton.
George B. Buckton.
Charles B. Clarke.
Dr. Lionel Beale.
Rev. Canon Tristram.

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lines. In some cases they appeared also in mercury lines. The velocities represented by the displacements of the lines were of the order of 4×10^5 metres per second for the hydrogen particles and $2{\cdot}5 \times 10^4$ metres per second for those of mercury. But it was found that, in general, the luminous mercury particles in the canal rays did not move, at any rate with a velocity greater than 100 metres per second. In these cases the canal rays appear to be due to non-luminous particles streaming through the mercury vapour and producing luminescence in the latter, probably by bombardment.

(5) A glass tube was sealed on to a canal-ray tube, at right angles to the direction of the rays. This tube was covered by a piece of optical glass as free as possible from strain. A very sensitive combination of Savart plate and Nicol prism was used to detect, if possible, any polarisation that might exist in the light from the rays in hydrogen. After eliminating reflections from the walls of the tube no polarisation could be recognised.

(6) The light produced by electrical discharge, in uniform tubes 3 or 4 cm. in diameter, was examined perpendicular to the direction of discharge, at various points between the electrodes and also behind the perforated cathode. It was found that the principal hydrogen lines were greatly broadened in those parts where the electric field is known to be of great intensity. For example, the luminous layer covering the cathode (the dark space being 0·5 to 4 cm.) gave hydrogen lines 0·4 Angström units in width, but the lines of the second hydrogen spectrum and certain air lines were not appreciably broadened. This broadening seems to be due mainly to motion of the particles rather than change of free periods, for it is found to the same extent behind the cathode in the canal rays. The broadening is so great that it is not possible with the instruments at the writer's disposal to determine the shift of these lines except to fix a superior limit of 0·1 A.U. to its possible magnitude. The amount is probably considerably less than this. On the other hand, the shift of the lines of the second spectrum of hydrogen is so small as to approach the limits of error, viz., 0·005 A.U. The mercury lines show no shift but a slight broadening.

The experiments thus show that any electrical analogue of the Zeeman effect is, under the above conditions, largely masked by a widening of the lines.

The work was carried out at the Cavendish Laboratory, Cambridge, during the past winter; and the writer's thanks are due to Professor J. J. Thomson and to Professor Liveing for the facilities kindly accorded to him.

On comparing this with fig. 23 above we see that the agreement is a close one. Curves *a*, *b*, and *c* of fig. 24 correspond to the following thicknesses as found by Meslin, 6 $\mu\mu$, 29 $\mu\mu$, and 41 $\mu\mu$; while *d* corresponds to Meslin's values for a thick plate. The Curve *d* is practically identical with the

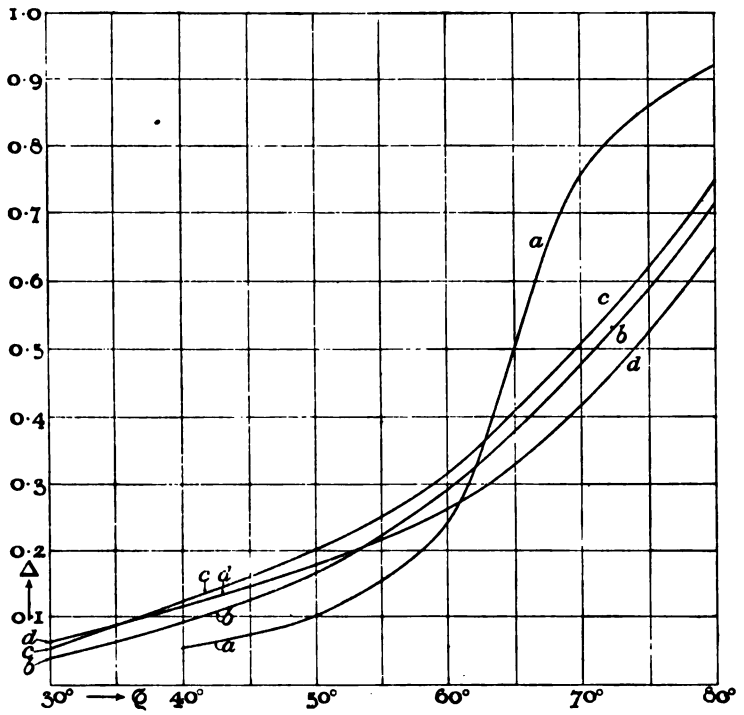

FIG. 24.

Curve 7 of fig. 23, while the Curves *c*, *b*, and *a* are very similar to Curves 5, 4, and 3 respectively. Taking $\lambda = 760\ \mu\mu$, the thickness of the metallic film corresponding to the Curves *a*, *b*, and *c* is $0{\cdot}008\,\lambda$, $0{\cdot}038\,\lambda$, and $0{\cdot}054\,\lambda$ respectively. Comparing these numbers with the values of ϵ_1, corresponding to the Curves 3, 4, and 5, we see that the thickness of the layer of transition is of the order assigned to it on p. 330 above.*

* The surface conditions of the various films and of the thick plate were probably different, so that the layer of transition would not be the same in each. These results, however, indicate that the thickness of the layer was of the same order in each case. The uncertainty as to the refractive index of the glass has most influence on the thinnest film.

Cancelled.

mean (true) values; but it would materially affect the other conclusions and especially the statement that the moist material attains to the full vapour tension of pure water when it contains a definite quantity of moisture. Unless very strong and direct evidence were forthcoming, we could not, after our own experience, believe that the whole of each "feed" of water driven over into the space containing the flannel was uniformly distributed as hygroscopic moisture throughout that substance before the vapour pressure was measured, or that no part of the final "feeds" was left as ordinary liquid water to exert its influence.

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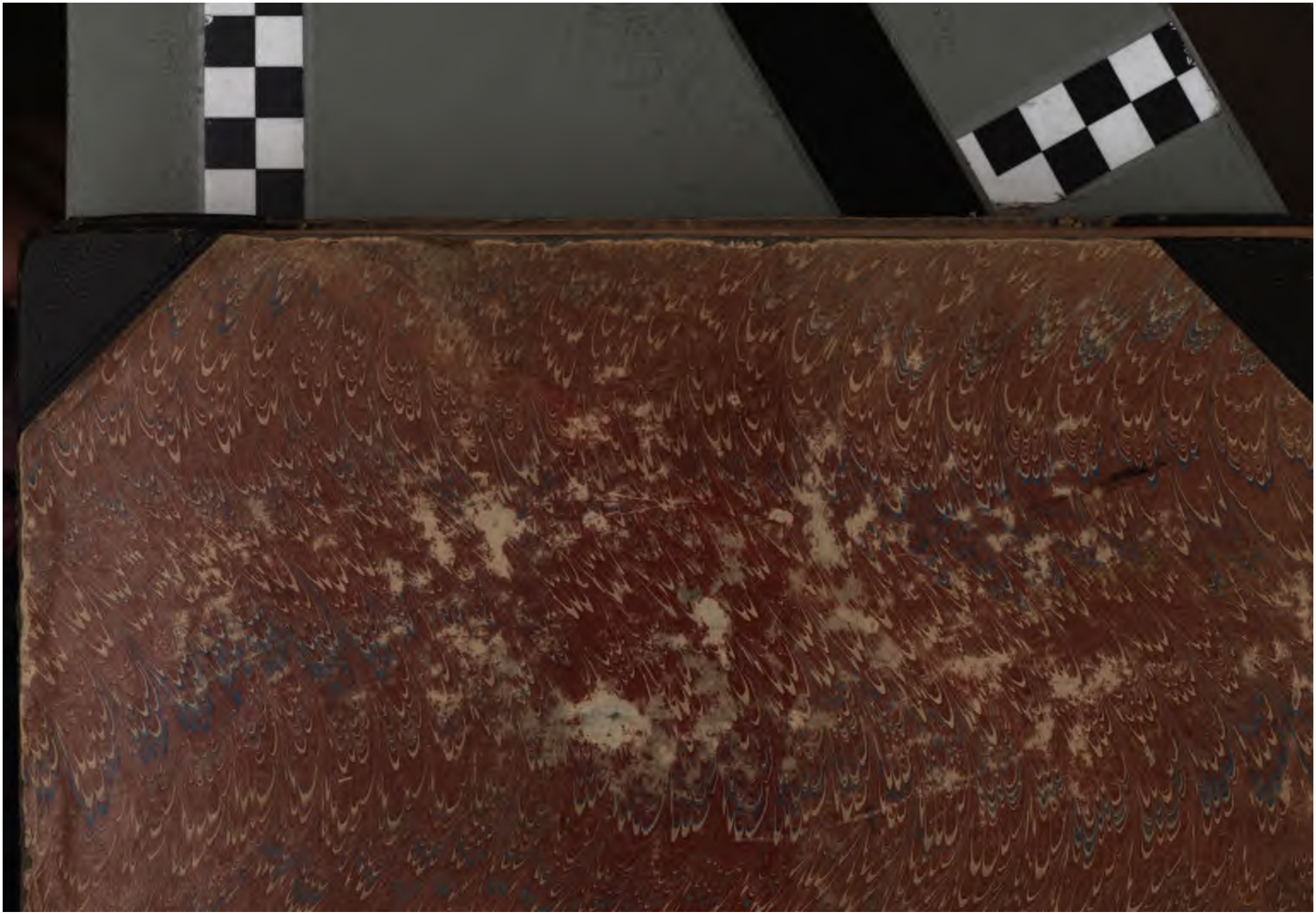
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